

# NATIONAL BUREAU OF STANDARDS REPORT

10 062

Progress Report  
on  
**THE CRYSTALLOGRAPHY OF OTHER BIOLOGICALLY  
SIGNIFICANT INORGANIC COMPOUNDS**



U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

## NATIONAL BUREAU OF STANDARDS

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NBS PROJECT

311.05-11-3110561

NBS REPORT

10 062

June 30, 1969

Progress Report  
on  
**THE CRYSTALLOGRAPHY OF OTHER BIOLOGICALLY  
SIGNIFICANT INORGANIC COMPOUNDS**

by  
Brian Dickens\*

\* Research Chemist, Dental Research Section, National  
Bureau of Standards, Washington, D. C. 20234

This investigation is part of the dental research program  
conducted by the National Bureau of Standards and is  
supported by the National Institute for Dental Research  
Collaborative Office.

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U.S. DEPARTMENT OF COMMERCE  
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THE CRYSTALLOGRAPHY OF OTHER  
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INTRODUCTION

Calcium and phosphate are present in vivo mainly as calcium hydroxyapatite (HA), which is the prominent topic of the symposium. Since hydroxyapatite is held together by ionic bonds, the ions in the structure can readily be replaced by other ions of roughly the same <sup>shape</sup> size, and charge. Some change in charge can be tolerated provided the crystal as a whole is kept electrically neutral. In a simple example, substitution of  $\text{Na}^+$  for  $\text{Ca}^{2+}$  could be compensated for electrically by substituting  $\text{SO}_4^{=}$  for  $\text{PO}_4^{=}$ . Thus compounds crystallizing in ionic lattices, and in the apatite structure in particular, need not be completely homogeneous as is well known. The apatite structure is apparently so stable that it is not only common among compounds with the same type of formula, but will also form as layers in a crystal interleaved with layers of differing stoichiometry, e.g., HA interlayered with octacalcium phosphate (see later). Substitutions in general, and in the HA structure in particular, can be envisioned on three levels:

- (i) interleaved layers (epitaxy)
- (ii) parts of one or more unit cells of related compounds replacing parts of the HA structure

(iii) substituted ions

It is therefore desirable to systematically study compounds related to HA with a view to revealing how the apatite structure can incorporate these substitutions or 'defects', and/or to gain enough structural knowledge to allow us to make predictions about the method of 'defect' incorporation.

The likelihood of epitaxy or other intergrowth can be considered from examinations of the crystal structures of appropriate compounds. Appropriate compounds, in turn, can be suggested from an observation of the types of coordination and bonding of ions. A formal evaluation of epitaxy has not yet been accomplished. In fact, only recently has a least squares computer program (Busing, 1968) been written to refine the various parameters required in a calculation of lattice energy from their initial estimates (by the method of steepest descents, using determined crystallographic parameters such as the cell dimensions and atomic positional parameters as observations). It may be feasible to calculate an approximation to the interfacial energy of two possibly epitaxial layers if the various energetic parameters above are "known". This, however, lies in the future.

Besides searching for structural features which may be significant in the incorporation of defects or nonstoichiometry into apparently homogeneous crystal structures, it is also significant to examine appropriate structures, which will probably be of hydrated salts (see below), for features which may be important in determining the identity of a precursor phase during crystallization. Hydrated salts may be important in the nucleation and growth of anhydrous species from aqueous environments for the following reasons (Dickens and Brown, 1968 ), mentioned briefly below:

- (i) For small particles such as the nucleating particles during crystallization, the surface energy is a large factor in determining the identity of the particles. The high energy attractions between ions are reduced, and the surface energy in an aqueous environment is lowered when the nucleus is formed from a highly/hydrated salt.
- (ii) Because of kinetic factors, hydrated salts often crystallize more rapidly than the anhydrous counterparts, even when the latter are thermodynamically more stable.



- (iii) Crystal growth poisons such as polyphosphates, magnesium and sugar, all of which are present in biological systems, apparently repress the growth of anhydrous calcium carbonates, and perhaps of HA, and allow hydrated forms to grow.
- (iv) Most nucleation processes are thought to be heterogeneous rather than homogeneous. In the case of biological mineralization such nucleation is thought to be on collagen and other proteins, which, because of their hydrophilic nature, would presumably reduce the surface energy of a hydrated salt to a lower value than that of an anhydrous salt.

In this chapter, we report on the contemporary structural knowledge of several compounds of interest. The structures of some of these have not been determined; some others are known except for the hydrogen atoms. In general much further work needs to be done.

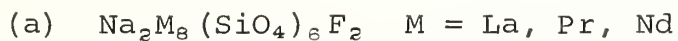
The compounds have been chosen to indicate the relationship of that particular structural type to HA. If a particular compound or ion sounds unlikely as a biological agent, a more acceptable compound with a high probability of having the same or a related crystal structure can often be thought of by



juggling the identities of the constituent ions while keeping the overall formula electrically neutral.

1. COMPOUNDS NOT ISOMORPHOUS WITH HYDROXYAPATITE BUT POSSIBLY RELATED TO IT. These compounds are relevant to hydroxyapatite in the context of possible ion substitution, unit cell substitution or interlayering.





Rare earth compounds with the general formula  $\text{Na}_2\text{M}_8(\text{SiO}_4)_6\text{F}_2$  have been prepared from molten fluxes by Ito (1967). The cell dimensions (Bowen, 1967; Swanson, McMurdie, Morris and Evans, 1969) are seen (Table 1) to be very closely related to those of HA (Posner, Perloff and Diorio, 1958) and fluorapatite (FA) (Naray-Szabo, 1930). The reciprocal lattice extinctions  $000l = 2n+1$  indicate the space groups  $\text{P6}_3$  or  $\text{P6}_3/\text{m}$ . The Ca ions in FA and HA are in positions 4f and 6h of space group  $\text{P6}_3/\text{m}$  (Table 2). The rare earth compounds probably have the space group  $\text{P6}_3$ , a subset of  $\text{P6}_3/\text{m}$ . Six rare earth ions thus probably occupy general positions in  $\text{P6}_3$  in a configuration like that of the 6 Ca ions in positions 6h of  $\text{P6}_3/\text{m}$  for FA and HA. The remaining two rare earth ions and the two Na ions probably occupy the 2b positions in  $\text{P6}_3$ , and thus lie in columns analogous to the columns of Ca ions in the 4f positions in FA and HA. Since the electrostatic repulsive energy of a chain of  $\text{M}^{3+} \dots \text{M}^{3+} \dots \text{Na}^+ \dots \text{Na}^+ \dots \text{M}^{3+}$  will be  $9 + 3 + 1 + 3 = 16$  units/unit cell (Table 3) whereas that of a chain  $\text{M}^{3+} \dots \text{Na}^+ \dots \text{M}^{3+} \dots \text{Na}^+ \dots \text{M}^{3+}$  will be  $3 + 3 + 3 + 3 = 12$  units/unit cell, these columns are expected to have Na and rare earth ions alternating. This may be relevant to the incorporation of foreign cations into hydroxyapatite.

Table 1

Comparison of $\text{Na}_2\text{M}(\text{SiO}_4)_6\text{F}_2$ unit cells with FA and HA			
	$\underline{a}$	$\underline{c}$	$\underline{z}$
$\text{Na}_2\text{La}_8(\text{SiO}_4)_6\text{F}_2$	9.6890(2) Å	7.1805(2) Å	1
$\text{Na}_2\text{Pr}_8(\text{SiO}_4)_6\text{F}_2$	9.5830(2)	7.0728(2)	1
$\text{Na}_2\text{Nd}_8(\text{SiO}_4)_6\text{F}_2$	9.51	7.02	1
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	9.37	6.88	1
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	9.432	6.881	1

Table 2

Comparison of  $\text{Na}_2\text{Mg}(\text{SiO}_4)_6\text{F}_2$  with  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  \*

Space group  $\text{P6}_3$

6c 1  $x, y, z$   
 $\bar{x}, y, .5+z$   
 $y, x-y, z$   
 $y, y-x, .5+z$   
 $y-x, \bar{x}, z$   
 $x-y, x, .5+z$

2b 3  $.33, .67, z$   
 $.67, .33, .5+z$

2a 3  $0, 0, z$   
 $0, 0, \bar{z}$

$\text{Na}_2\text{Mg}(\text{SiO}_4)_6\text{F}_2$

6 M in (6c) with  $x \approx .25$ ,  
 $y \approx 0$ ,  $z \approx .25$

2 M in (2b) with  $z \approx 0$ .  
2 Na in (2b) with  $z \approx .5$

24 O in general position (6c)

2 F in (2a) with  $z \approx .25$

Space group  $\text{P6}_3/\text{m}$

6h m  $x, y, .25$   
 $\bar{x}, \bar{y}, .75$   
 $y, x-y, .25$   
 $y, y-x, .75$   
 $y-x, x, .25$   
 $x-y, x, .75$

4f 3  $.33, .67, z$   
 $.67, .33, .5+z$   
 $.67, .33, \bar{z}$   
 $.33, .67, .5-z$

2a  $\bar{6}$   $0, 0, .25$   
 $0, 0, .75$

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$

6 Ca in (6h) with  $x = .2466$ ,  
 $y = .0031$

4 Ca in (4f) with  $z = .0014$

12 O in general position  
with  $x = .3433$ ,  $y = .2579$   
 $z = .0705$

6 O in (6h) with  $x = .3283$   
 $y = .4846$ ,  $z = .25$

6 O in (6h) with  $x = .5876$   
 $y = .4652$ ,  $z = .25$

2 F in (2a)

\* Kay, Young and Posner (1964).

Table 3

Comparison of electrostatic energies  
for differently ordered chains

$$\begin{array}{ccccccc}
 \begin{array}{c} 3+ \\ M \end{array} & \dots\dots M & \begin{array}{c} 3+ \\ \dots\dots Na^+ \end{array} & \dots\dots Na^+ & \dots\dots M & \begin{array}{c} 3+ \\ \dots\dots M \end{array} \\
 9 & 3 & 1 & 3 & & \\
 & & & & & = 16 \text{ total}
 \end{array}$$

$$\begin{array}{ccccccc}
 \begin{array}{c} 3+ \\ M \end{array} & \dots\dots Na^+ & \begin{array}{c} 3+ \\ \dots\dots M \end{array} & \dots\dots Na^+ & \dots\dots M & \begin{array}{c} 3+ \\ \dots\dots M \end{array} \\
 3 & 3 & 3 & 3 & & \\
 & & & & & = 12 \text{ total}
 \end{array}$$

(b)  $\text{CaK}_3\text{H}(\text{PO}_4)_2$

The structure of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  (Frazier, Smith, Lehr and Brown, 1962; Brown and Fowler, 1967) is very closely related to that of  $\text{NaK}_3(\text{SO}_4)_2$  (glaserite). The formal relation between the type structure  $\text{NaK}_3(\text{SO}_4)_2$  and HA has been discussed by Wondratschek (1963).

$\text{CaK}_3\text{H}(\text{PO}_4)_2$  is unusual in that although it contains a phosphate group with an acid hydrogen, it is formed from solutions with a pH of 10-11. Presumably the packing in the structure is so efficient that the structure is able to remove a proton from such an alkaline environment in order to achieve the correct charge balance. In water,  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  hydrolyzes to HA. It has not been found in physiological situations, but here is relevant/because of its structural relationship to HA.

The usual unit cells of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ ,  $\text{NaK}_3(\text{SO}_4)_2$  and HA are shown in Table 4 and are redefined in Table 5 to bring out their close correspondence.

That  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  and  $\text{NaK}_3(\text{SO}_4)_2$  must have similar structures can be seen from

- (1) the similarities of their formulae except for the H.



Table 4

The Unit Cell Dimensions of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ ,

$\text{NaK}_3(\text{SO}_4)_2$  and HA

	$\text{CaK}_3\text{H}(\text{PO}_4)_2$	$\text{NaK}_3(\text{SO}_4)_2$	$\text{Ca}_5\text{OH}(\text{PO}_4)_3$ (HA)
a	9.93 Å	5.66 Å	9.43 Å
b	5.72	5.66	9.43
c	7.44	7.33	6.88
$\alpha$	90°	90°	90°
$\beta$	92.3	90	90
$\gamma$	90	120	120
z	2	1	2
space-group	$\text{C}^2/\text{m}$	$\text{P}\bar{3}\text{m}1$	$\text{P}6_3/\text{m}$

Table 5

The Unit Cells from Table 4, Redefined

	$\text{Ca}_3\text{K}_9\text{H}_3(\text{PO}_4)_6$	$\text{Na}_3\text{K}_9(\text{SO}_4)_6$	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
a	9.93 Å	9.80 Å	9.43 Å
b	9.92	9.80	9.43
c	7.44	7.33	6.88
$\alpha$	91.6°	90°	90°
$\beta$	91.6	90	90
$\gamma$	120	120	120

- (2) The similar dimensions of their ions

Na ionic radius =  $0.96 \text{ \AA}$

Ca ionic radius =  $0.99 \text{ \AA}$

K ionic radius =  $1.33 \text{ \AA}$

P-O bond distance =  $1.56 \text{ \AA}$

S-O bond distance =  $1.44 \text{ \AA}$

- (3)  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  is pseudo-trigonal in morphology, twinning, cell dimensions and in the intensities of supposedly non-equivalent reflections on all layers. The trigonal space-group which will most easily accommodate one formula weight of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  is  $\text{P}\bar{3}\text{m1}$ , which is the space-group of  $\text{NaK}_3(\text{SO}_4)_2$ . The actual space-group of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ ,  $\text{C}^2/\text{m}$ , is a subgroup of  $\text{P}\bar{3}\text{m1}$ .
- (4) the x-ray intensities of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  indicate a subcell with the heavy atoms at the corners as is found in  $\text{NaK}_3(\text{SO}_4)_2$ .
- (5) the x-ray powder patterns of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  and  $\text{NaK}_3(\text{SO}_4)_2$  are very similar.

Thus, the  $\text{NaK}_3(\text{SO}_4)_2$  structure can be used as a first approximation to the actual structure of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  with the exception of H, which is probably to be found <sup>in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$</sup>  across the O.....O close approach, i.e., across a center of symmetry in  $\text{NaK}_3(\text{SO}_4)_2$ . This hydrogen bond will destroy the three-fold axis of the  $\text{PO}_4$  group, but will keep the mirror plane of  $\text{C}^2/\text{m}$ . By analogy with other structures containing an O-H...O hydrogen bond across a nominal center of symmetry, the hydrogen is probably disordered about the center of symmetry. This conclusion is supported by IR and NMR evidence (Brown and Fowler, 1967).

In the  $\text{NaK}_3(\text{SO}_4)_2$  structure (Fig. 1) there are columns of  $\text{SO}_4$  groups and K ions related by a  $\bar{3}$  axis. Thus, adjacent columns have the  $\text{SO}_4$  groups pointing "up" and "down". The remaining ions, Na and K, are packed into columns designated by small circles in Figure 1. The formula balance is kept because there are twice as many  $\text{SO}_4/\text{K}$  columns as there are Na/K columns.

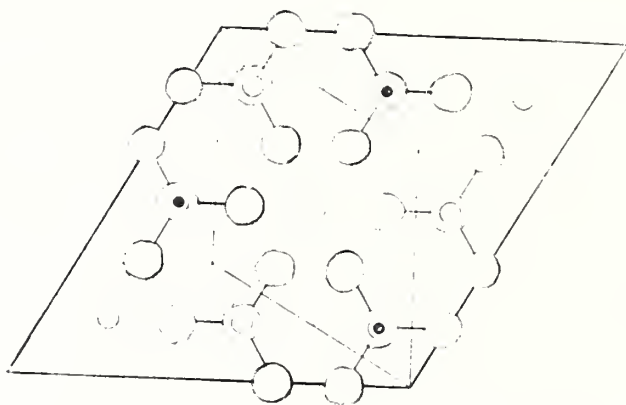


Figure 1. The crystal structure of glaserite,  $\text{NaK}_3(\text{SO}_4)_2$ .

The columns with the dark dots may be considered to have the O of the  $\text{SO}_4$  group above the S on the three-fold axis, the others have the O below the S. The light line corresponds to the real unit cell, the heavy line is the refined cell. The small circles are columns of Na and K ions. One of these columns may be considered to have replaced the  $\text{OH}^-$  column in HA.

The effect of changing the sign of the ions in the central column may be seen by comparing the structure of  $\text{NaK}_3(\text{SO}_4)_2$  with that of HA (Fig. 2). In HA the Ca ions have been pulled in by the  $\text{OH}^-$ , and the  $\text{PO}_4$  groups have moved out so that they can coordinate to the Ca's through their oxygens while keeping the repulsion with  $\text{OH}^-$  within tolerance. Further, the  $\text{PO}_4$  groups have tilted over about  $35^\circ$  which puts two oxygens near the centers of two Ca triangles (Fig. 3), in the Ca/O configuration found in aragonite (Bragg, 1924) and each of puts the other two oxygens near the center of a Ca...Ca line in the configuration found in calcite (Bragg, 1913).

$\text{CaK}_3\text{H}(\text{PO}_4)_2$  could exhibit epitaxial growth on HA or interchange with HA on a unit cell level and thus have relevance to the mechanism of crystal growth, to the poisoning of crystal growth and in the incorporation of impurities and defects.

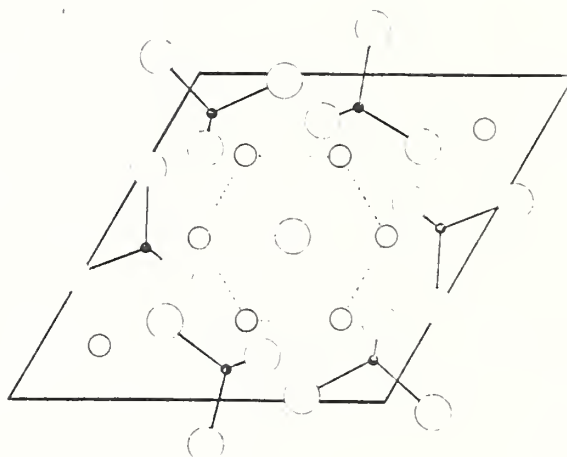


Figure 2. The crystal structure of HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , projected down the  $\underline{c}$  axis.



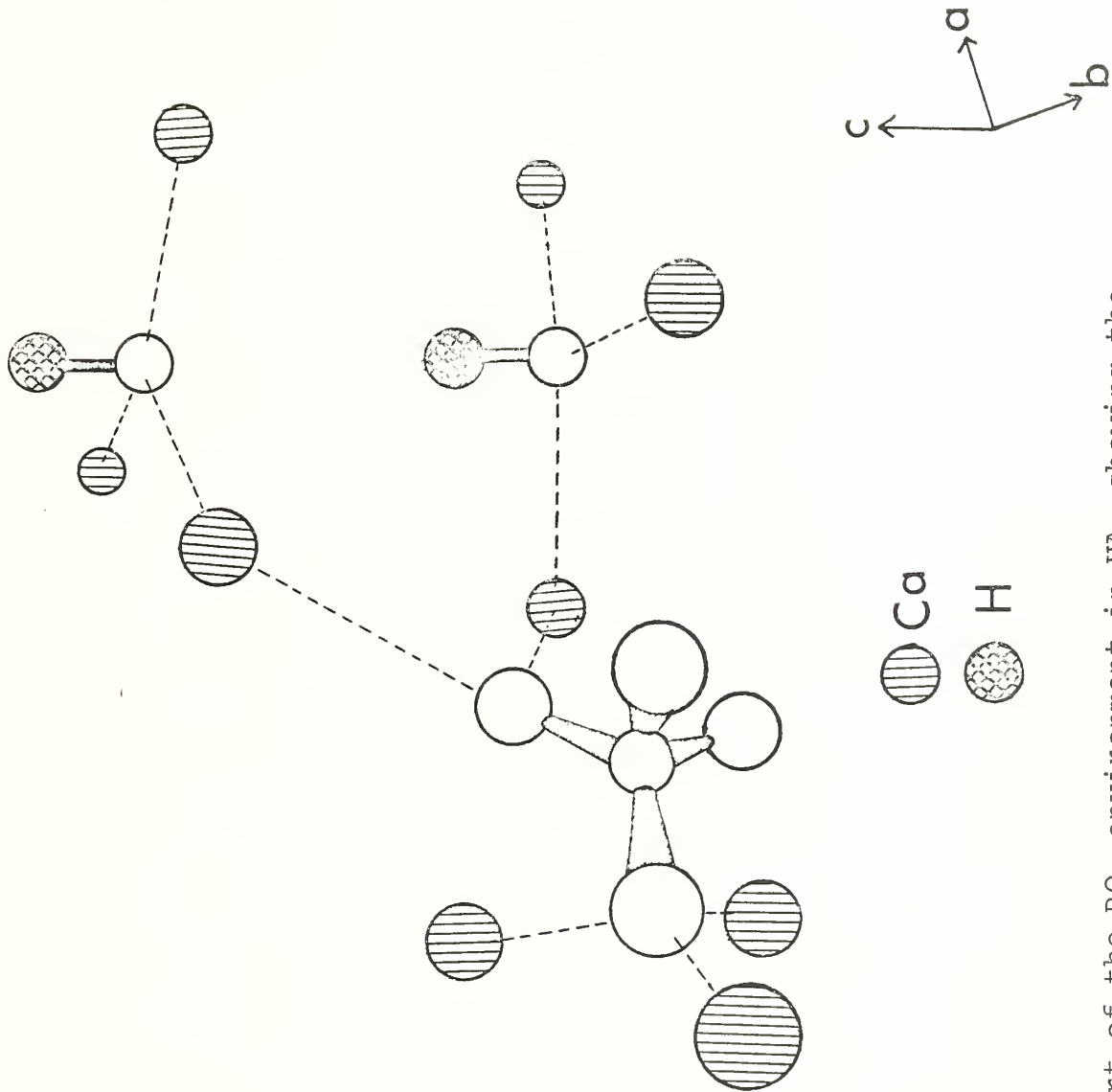


Figure 3. Part of the  $\text{PO}_4$  environment in HA, showing the similarity in  $\text{Ca}\cdots\text{O}$  coordinations in HA, calcite and aragonite.

(c) Silico-carnotite  $\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$

Silico-carnotite, which is apparently named more after its discoverer, Carnot, than by analogy with the mineral carnotite, is found in basic slags rich in phosphorus. Since it is readily soluble in dilute acids, it has been used for many years directly as a plant fertilizer. It has been reported to exist over a range of composition of about 55% to 83%  $\text{Ca}_3(\text{PO}_4)_2$  by weight at 1125°C (Nurse, Welch and Gutt, 1959) and has been found in several high temperature investigations (Nurse, et al, 1959; Berak and Wojciechowska, 1956; Vol'fkovich, Illarionov, Ozerov and Remen, 1960) of the  $\text{Ca-PO}_4\text{-SiO}_4$  system. Since stoichiometric silico-carnotite is unstable below about 750° (Nurse et al, 1959) it must be preserved by quenching. Keppler (1968) has performed microprobe analyses on various crystals of silico-carnotite and has concluded that it is a definite compound.

The crystallographic properties of a representative specimen are given in Table 6. (Riley and Segnit, 1948; Tromel Dickens and Brown, 1969) and Zaminer, 1959; Keppler, 1968)/. There is good correspondence dimensions between the unit cell /of hydroxyapatite and silico-carnotite, and especially between the volumes of one formula weight (Table 7). Although silico-carnotite has the same cation/anion ratio (5/3) as the garnets  $(A_3B_2(XO_4)_3)$  where A and B are cations and  $XO_4$  is an anion), the garnet structure is/too dense for silico-carnotite since the garnets invariably have for B some small cation which can form B.....O distances of about  $2 \text{ \AA}$ . In the garret  $Ca_3Al_2(SiO_4)_3$  (Abrahams and Geller, 1958) B is Al, Ca....O distances are usually greater than  $2.3 \text{ \AA}$ . which forms Al.....O distances of  $1.95 \text{ \AA}$ ./

Table 6

Silico-carnotite data



$$N_\alpha = 1.641 \parallel \underline{c}, N_\beta = 1.655 \parallel \underline{b}, N_\gamma = 1.663 \parallel \underline{a},$$

measured on {001} plates

orthorhombic, space-group Pnma or Pn2<sub>1</sub>a

$$\underline{a} = 6.737 \pm .001, \underline{b} = 15.508 \pm .004, \underline{c} = 10.132 \pm .002 \text{ \AA}$$

Table 7

A Comparison of the Unit Cells of HA, a Garnet,  
Silico-Carnotite and Pyromorphite

	HA $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Garnet $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	Silico- carnotite (a) $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$	Pyromorphite $\text{Pb}_5(\text{PO}_4)_2\text{SiO}_4$
<u>a</u>	9.43 Å	11.87 Å	15.508 Å	9.79 Å
<u>b</u>	9.43	11.87	10.132	9.79
<u>c</u>	6.88	11.87	6.737	7.32
$\gamma$	120°	90°	90°	120°
vol.	530 Å <sup>3</sup>	1672 Å <sup>3</sup>	1059 Å <sup>3</sup>	608 Å <sup>3</sup>
z	2	8	4	2
density	3.14	3.58	3.10	7.20
vol. of 1 F.wt	265 Å <sup>3</sup>	209 Å <sup>3</sup>	265 Å <sup>3</sup>	304 Å <sup>3</sup>

$$a_{\text{sc}} = 15.47 \text{ Å} \quad \sqrt{3}a_{\text{HA}} = (2d_{100}) = 16.34 \text{ Å}$$

(a) with permuted axes

Dickens and Brown (1969) have very recently determined the crystal structure ( $R = 0.05$ ) of silico-carnotite using a crystal from sample D (British Museum sample 1919,64) in Riley and Segnit's paper (1948). Silico-carnotite was expected to follow in the HA-glaserite series as a member where the structure is essentially the HA structure with an empty column where the OH's are found in HA. The actual structure of silico-carnotite may be considered to be a distorted form of the above. The column Ca's in HA are represented by a Ca zig zag in silico-carnotite. The six  $\text{Ca}(2)/\text{PO}_4$  chains along  $\underline{c}$  (surrounding the OH column) in HA are represented by four  $\text{Ca}/\text{PO}_4$  and two  $\text{Ca}/\text{SiO}_4$  in silico-carnotite chains. A further distortion/is that the Ca's in the  $\text{SiO}_4$  chain have been pulled in towards the OH site in HA to form a central zig zag of cations. The structure of silico-carnotite thus also approaches the  $\text{NaK}_3(\text{SO}_4)_2$  structure and is intermediate between HA and  $\text{NaK}_3(\text{SO}_4)_2$ .

The structure principles found in silico-carnotite may be used in an appropriate calcium phosphate ( $\text{Ca}_4\text{Na}(\text{PO}_4)_3$  is one possibility) to allow the stoichiometry and properties of HA to change locally.

$\text{Pb}_5(\text{PO}_4)_2\text{SiO}_4$  (pyromorphite) has been reported by Wondratschek (1963) from x-ray data to be hexagonal with cell dimensions (Table 7) similar to those of hydroxyapatite. Presumably the lead atoms are in a hexagonal array perpendicular to c and either dominate the scattering so that deviations from hexagonal symmetry because of the non-equivalence of the  $\text{PO}_4$  and  $\text{SiO}_4$  groups are unnoticed, or the  $\text{PO}_4$  and  $\text{SiO}_4$  groups are statistically disordered. The formula of  $\text{Pb}_5(\text{PO}_4)_2\text{SiO}_4$  relates it to silico-carnotite, and it may have a closely related structure, perhaps made hexagonal or more nearly so by the effect of the increased size ( $\text{Pb}^{2+} = 1.20 \text{ \AA}$ ,  $\text{Ca} = 0.99 \text{ \AA}$ ) of the cation. The structure of  $\text{Pb}_5(\text{PO}_4)_2\text{SiO}_4$  is of great interest, and would be best determined by neutron diffraction.

(d) Tetracalcium phosphate,  $\text{Ca}_4\text{O}(\text{PO}_4)_2$ , TCP

Tetracalcium phosphate (Bookey, Richardson and Welch, 1952; Tromel, Fix and Fritze, 1961; Brown and Epstein, 1965) or Hilgenstockite, is prepared at high temperatures in systems free of water. It may not be found in vivo but may have a structural relationship to HA (Table 8) where it can be seen that the cell volume of HA and the a and c axes and hence the (010) faces of the two compounds are very closely related.



Table 8

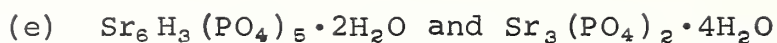
A Comparison of the Unit Cells of  
Hydroxyapatite and Tetracalcium Phosphate

	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	$\text{Ca}_4\text{O}(\text{PO}_4)_2$
<u>a</u>	9.432 Å	9.462 Å
<u>b</u>	9.432	11.965
<u>c</u>	6.881	7.023
$\gamma$	120°	90.8°
vol.	530 Å	795 Å <sup>3</sup>
	Space group	P2 <sub>1</sub>

$d_{100} \text{ (HA)} \times 1.5 = 12.27 \text{ Å}$   
 $530 \text{ Å}^3 \times 1.5 = 795 \text{ Å}^3$

Although the crystals are nearly always twinned, we have collected x-ray data from an apparently untwinned single crystal. Statistical tests on the quasi-unitary structure factors indicate that the space group is non-centrosymmetric, and must therefore be  $P2_1$  from the x-ray extinctions. We have tried to solve the structure by superposition techniques, using an unsharpened Patterson map, but obtained a trial structure for the Ca and P atoms which would not refine satisfactorily. This trial structure has four layers roughly equally spaced along  $b$ . We plan further effort in the solution of the structure using statistical methods on the quasi-normalized structure factors (Dickinson, Stewart and Holden, 1966).

TCP takes up  $CO_2$ , especially at high temperatures when the  $O=$  presumably becomes  $CO_3^{2-}$ . This is of considerable interest to the problem of carbonate-apatites, and suggests that carbonation of apatite can take place by making an  $OH^-$  into  $HCO_3^-$  or  $CO_3^{2-}$  and expelling water if necessary. Since two cells of TCP can, on spatial considerations, readily replace three cells of HA, TCP may fit easily into the HA lattice and thus substitution of TCP for HA may provide a mechanism of defect incorporation and/or carbonate incorporation in HA.



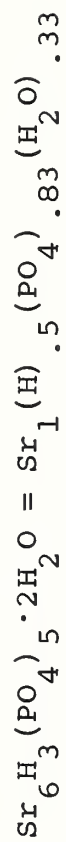
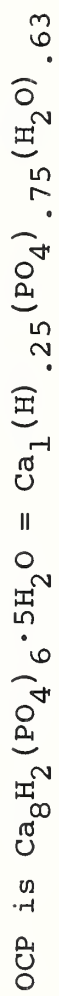
These two compounds (Collin , 1959, 1960, 1964, 1966) are of interest because of the mechanism of incorporating  $\text{Sr}^{90}$  in the body. Also,  $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$  has been shown to immediately precede the formation of SrHA in vitro and there is evidence, quoted below, that the same may be true in vivo.  $\text{Sr}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$  may be related to the "amorphous phase" (Eanes, Gillesen and Posner, 1965, 1967; Weber, Eanes and Gerdes, 1967) found in the precipitation of calcium phosphates from aqueous solution.

In an examination (Johnson, Armstrong and Singer, 1966) of the tooth enamel of rats fed on a strontium-rich diet, the cell dimensions of the hydroxyapatite present were found to have increased from  $\underline{a} = 9.47$ ,  $\underline{c} = 6.86 \text{ \AA}$  in enamel from Sr-poor animals to  $\underline{a} = 9.48 \text{ \AA}$ ,  $\underline{c} = 6.91 \text{ \AA}$  in Sr-rich animals. Extra lines in the powder patterns of the tooth enamel could be attributed to  $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$ .  $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$  otherwise has a powder pattern very similar to HA and, because of its Sr/P ratio of 1.2, could lower the apparent stoichiometry of (Ca, Sr) HA by interlayered growth in the way suggested (Brown, Smith, Lehr and Frazier, 1962) for octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , (OCP). The formulae of  $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$

and OCP are compared in Table 9. The Sr salt is obviously more acidic than OCP and contains less water.  $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$  is the sole solid phase formed (Collin, 1966) (at pH 7.7) when 2.3 equivalents of  $\text{Sr}(\text{OH})_2$  are added to 1 equivalent of  $\text{H}_3\text{PO}_4$ . It often forms as a disordered intergrowth of crystals from aqueous solution.

$\text{Sr}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$  is formed (Collin, 1966) when more than 2.6 equivalents of  $\text{Sr}(\text{OH})_2$  are added to 1 equivalent of  $\text{H}_3\text{PO}_4$ , and is stable for many days at  $0^\circ\text{C}$ . At  $25^\circ\text{C}$  and  $37^\circ\text{C}$  it very easily changes into SrHA (Collin, 1966). Its high degree of hydration make it of great interest. It has a variable water content as does OCP. The strong reflection at  $2\theta = 6^\circ$  ( $\text{CuK}\alpha$  radiation) is dependant on the degree of hydration and suggests that the structure has a layer structure with a repeat distance of about  $14 \text{ \AA}$  (Collin, 1964). OCP has a layer structure with a repeat of about  $18.7 \text{ \AA}$ .

Table 9



Thus  $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  is of interest to biological mineralization both as a possible candidate for a direct analogy to amorphous calcium phosphate, and as another structure which can incorporate several water molecules with alkaline earth and phosphate ions perhaps arranged in layers. Other examples of the latter are  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .

(f) Octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , OCP

The possible importance of OCP in reducing the apparent Ca/P ratio of CaHA and in the growth mechanism of HA has been discussed by Brown (1966). The unit cells of OCP and HA are compared in Table 10. Since the b, c and  $\alpha$  dimensions are very similar in the two compounds, their unit cells can easily share a common face.

The structure of OCP has been determined (Brown, 1962) but the hydrogen atoms have not been located because the x-ray data contain the effect of large corrections for absorption. Good large (0.1-0.2 mm) single crystals of OCP are very difficult to grow. We are attempting to grow suitable single crystals in order to recollect the data. We are also reprocessing the photographic x-ray data collected earlier and plan to describe the structure in much more detail when the fine details are better known. The structure of OCP is shown in Figure 4 and consists of apatitic layers between  $x = -.25$  to  $+.25$  interlayered by a hydrated layer with some Ca and  $\text{PO}_4$  ions.

Table 10

A Comparison of the Unit Cells of OCP and HA

	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (OCP)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA)
<u>a</u>	19.87 Å	9.42 Å
<u>b</u>	9.63	9.42
<u>c</u>	6.87	6.88
$\alpha$	89° 17'	90°
$\beta$	92° 13'	90°
$\gamma$	108° 57'	120°



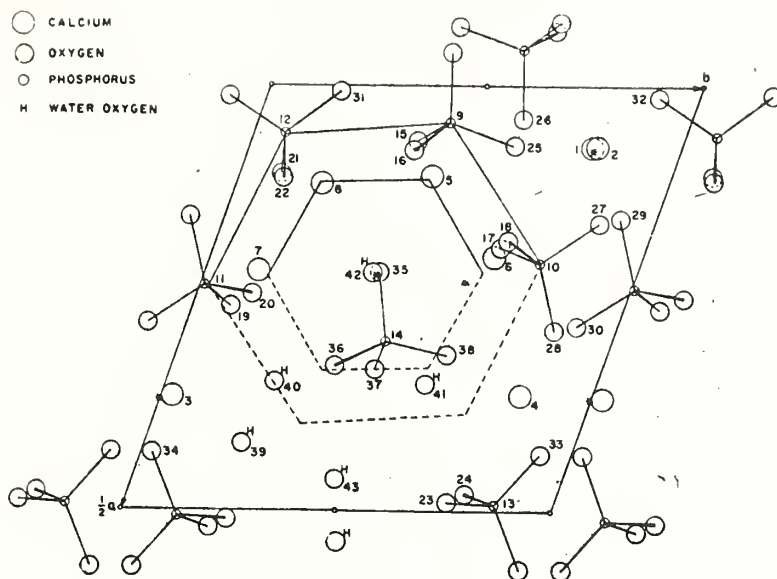


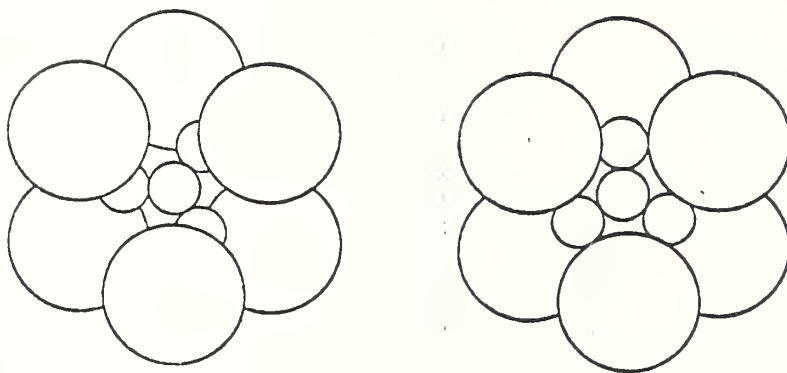
Figure 4. The crystal structure of octacalcium phosphate.

The corners of the two hexagons are the phosphorus and calcium positions as they occur in projection in HA. (The hexagon in HA is a trigonal antiprism in three dimensions.) Two Ca ions and two  $\text{PO}_4$  groups occur at each level of the trigonal antiprism in OCP. The environments of the Ca ions are very similar to those of the corresponding ions in HA. The OH groups in columns in HA have been replaced by the O(42) water molecule and O(35) of the P(14)  $\text{PO}_4$  group. The O(41) water has replaced a Ca ion in HA and presumably hydrogen bonds to the groups that Ca would have bonded to electrostatically with roughly similar distances ( $\text{Ca}-\text{O} \approx 2.4 \text{ \AA}$ ,  $\text{O}-\text{H} \dots \text{O} = 2.5 \dots 2.8 \text{ \AA}$ ). The Ca(1) and Ca(2) ions in OCP are almost exactly analogous to the column Ca's in HA. The other column has been distorted considerably with Ca(3) roughly in the same position as a column of Ca's in HA but <sup>with</sup> Ca(4) moved by about  $1.5 \text{ \AA}$  along the b axis to bond to O(41) which has replaced a Ca ion in the HA structure. The detailed atomic arrangement around these <sup>Ca</sup> ions is part way between the environment of the Ca (5,6,7,8) ions and the environment of the Ca(1,2) ions. <sup>R</sup> Layered intergrowth of OCP and HA has been observed directly and the crystal habit of HA has been correlated with that of OCP by topotactic change (Brown, Smith, Lehr and Frazier, 1962).

2. CALCIUM CARBONATES. The calcium carbonates are the other great body of biological minerals. The anhydrous forms have been found in the shells of marine life (K. M. Wilbur, 1964) and in humans in gallstones (Sutor and Wooley, 1968). Bone can contain (Neuman and Neuman, 1958) up to 6% carbonate ion.

(a) Calcite,  $\text{CaCO}_3$

Calcite is the most stable form of  $\text{CaCO}_3$  at normal temperatures. It is abundant in nature in such forms as the shells of several sea creatures, including oysters, and in gallstones, as well as a mineral. It is the final form precipitated from aqueous solutions at room temperature in the absence of crystal growth poisons such as polyphosphates,  $\text{Mg}^{2+}$  and sugars. It crystallizes in a hexagonal unit cell,  $\underline{a} = 4.989$ ,  $\underline{c} = 17.062 \text{ \AA}$ , spacegroup  $R\bar{3}c$ , and the structure is well known (Bragg, 1913; Sass, Vidale and Donohue, 1957). The oxygens are hexagonally closed packed and the Ca's are in octahedral coordination. As shown in Figure 5, each oxygen is coordinated to two Ca's. Calcite is isomorphous with  $\text{NaNO}_3$  and with the carbonates of Mg, Mn, Fe, Zn, Cd and Co, which are all small ions with ionic radii in the / 0.65 to 1.0  $\text{\AA}$ .



A. CO<sub>3</sub> environment in calcite. B. CO<sub>3</sub> environment in aragonite.  
From Bragg (1924).

Figure 5.

(b) Aragonite,  $\text{CaCO}_3$

Aragonite is the next most stable form of  $\text{CaCO}_3$  at room temperature. It is denser than calcite and presumably is more stable than calcite at low temperatures and/or high pressures. When heated it changes into calcite (Subba Rao and Yoganarashimhan, 1965) with the [001] of aragonite becoming the [0001] of calcite and [100] and [110] of aragonite being parallel to  $[01\bar{1}0]$  and  $[10\bar{1}0]$  respectively of calcite (Dasgupta, 1964). Thus, during the transition the  $\text{CO}_3$  group in aragonite is rotated  $30^\circ$  about  $c$  and moved to halfway between the Ca layers. The Ca layers must also change to become an ABCABC sequence in calcite instead of the ABABAB sequence in aragonite. <sup>P</sup> Aragonite is found in coral, clams and gallstones, and is isomorphous with the carbonates of Ba, Sr and Pb. Aragonite is precipitated preferentially to calcite from aqueous environments at temperatures above about  $40^\circ\text{C}$ . The unit cell is compared to that of calcite in Table 11. The structure (Fig. 6) is known formally (Bragg, 1924) but apparently not well by modern standards.

Table 11

A Comparison of the Unit Cells of Calcite and Aragonite

	Calcite	Aragonite*
<u>a</u>	4.989	4.959
<u>b</u>	4.989	7.968
<u>c</u>	17.062	5.741
$\gamma$	120°	90°

$4.989 \times 1.7321 = 8.64 \text{ \AA}$  (orthohexagonal description of calcite  
compare with b (aragonite = 7.968)  
 $5.72 \times 3 = 17.16 \text{ \AA}$  (comparison of c (aragonite) with c calcite)

\*ASTM card 5-0453

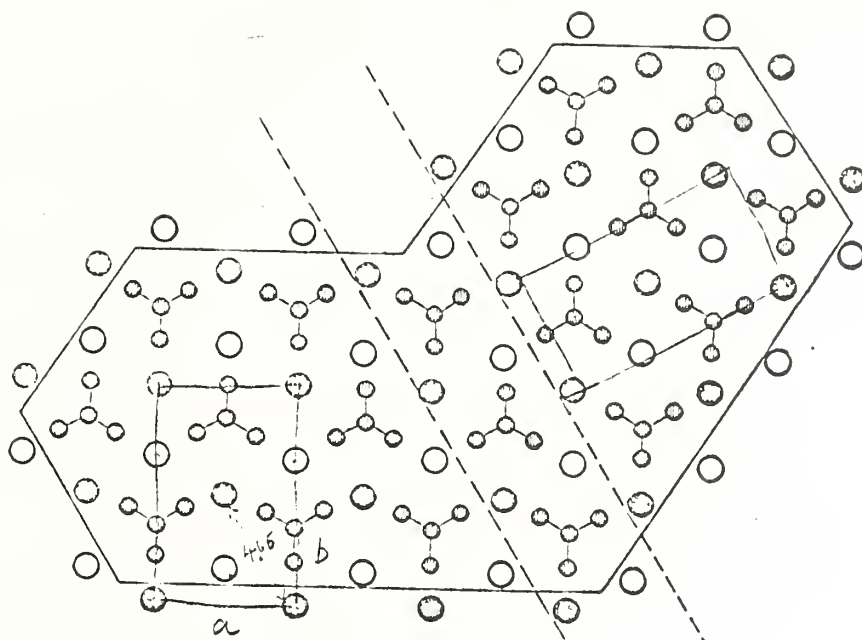


Figure 6. Crystal structure of aragonite perpendicular to  $\underline{c}$  (twinned on  $(110)$ ). From Bragg (1924).

In aragonite, the oxygens are coordinated equally to three Ca's instead of two as in calcite (Fig. 5). Aragonite twins easily in the way explained by Bragg and has been reported (Hiragi, Kachi, Takeda and Nakanishi, 1966) to exist in fine particles ( $0.5 - 1.0 \mu$ ) which have, at least in part, a superstructure (Fig. 7) with space-group Pbca and cell dimensions  $\underline{a} = 8.420$ ,  $\underline{b} = 9.385$ ,  $\underline{c} = 5.741$ . The relationship of the superstructure ( $\underline{As}$ ,  $\underline{Bs}$ ,  $\underline{Cs}$ ) to the normal structure ( $\underline{a}$ ,  $\underline{b}$ ,  $\underline{c}$ ) of aragonite is  $\underline{As} = \underline{a} - \underline{b}$ ,  $\underline{Bs} = 3/2\underline{a} + 1/2 \underline{b}$ ,  $\underline{Cs} = \underline{c}$ .

(c) High pressure phases of  $\text{CaCO}_3$

X-ray diffraction studies (Davis, 1964) at high pressures on powdered calcite (calcite I) have indicated the existence of two more phases of  $\text{CaCO}_3$ .  $\text{CaCO}_3$  (II), a modified calcite type, is probably isostructural with  $\text{KNO}_3$  (III) (Davis, 1963) which is/related to calcite (Table 12) but has only unidirectional order of the  $\text{NO}_3^-$  ion (about the 3-fold axis).

Calcite I is considered to transform into Calcite II at about 15.5 Kb pressure. Calcite III is stable at higher pressures (about 17.6 Kb to 27 Kb). Its powder pattern has been indexed (Davis 1964) as a  $\text{KNO}_3$ -IV aragonite type (Table 13) though this is still not certain.



Table 12

Comparison of the Proposed Unit Cells of the  
High Pressure Forms  $\text{KNO}_3$  (III) and  $\text{CaCO}_3$  (II) With Calcite

Calcite (I)	$\text{KNO}_3$ (III)	$\text{CaCO}_3$ (II)
4.989 Å	5.44 Å	4.98 Å
17.062	18.25	16.83

Table 13

Comparison of the High Pressure Forms

KNO<sub>3</sub> (IV) and Calcite (III) with Aragonite

Aragonite	KNO <sub>3</sub> (IV)	Calcite (III)
5.741 Å	11.04 Å	8.90 Å
4.959	8.36	8.42
7.978	7.40	7.14

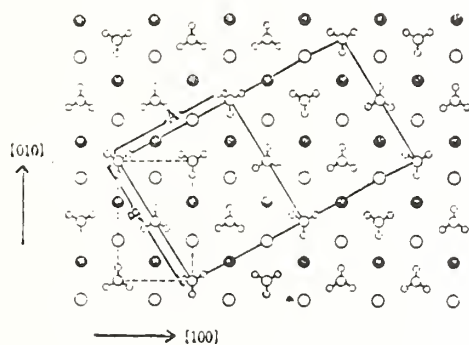


Figure 7. The (001) plane projection of the model for the superstructure, including atoms from 0 to  $\underline{c}/2$ . The solid lines show the unit cells of the superstructure, and the broken lines a unit cell of normal aragonite. The / is no longer periodic within the broken lines. From Hiragi, Kachi, Takada and Nakanishi (1966).

The structures of the disordered  $\text{KNO}_3$  and  $\text{CaCO}_3$  forms are still not known. These disordered forms may be important in understanding the mechanisms of defect incorporation in calcium carbonates and in studying the kinetics of calcareous reactions.

(d) Vaterite,  $\text{CaCO}_3$

Vaterite has been found as a mineral (McConnell, 1960), in the repaired part of mineralized tissue (Wilbur and Watabe, 1964) and in gallstones (Meier and Moenke, 1961). It has been recognized as the end member of the series of rare earth fluoride carbonate-calcium carbonate series bastnaesite-roentgenite-synchisite...vaterite (Donnay and Donnay, 1953). Structures have been given by Meyer (1959) and Kahmi (1963). Vaterite often grows in a spherulitic form; spherulitic vaterite has been discussed by Donnay and Donnay (1967). Kahmi used crystals which under high magnification could be seen to be aggregates of uniformly oriented hexagonal plates. Meyer proposed a structure in an orthohombic space group with<sup>a</sup> primitive ortho-hexagonal unit cell. His space

group and structure are incompatible with the results of other workers who have assigned vaterite to the hexagonal crystal system.

Optical studies (Bunn, 1945) had shown that the  $\underline{c}$  axis of the hexagonal system must be in the plane of the  $\text{CO}_3$  group. (This is presumably the major difference between vaterite and calcite and aragonite. The  $\text{CO}_3$  groups are perpendicular to the hexagonal axis in the case of calcite and <sup>to</sup> the corresponding pseudo hexagonal  $\underline{c}$  axis in the case of aragonite.) The vaterite structure can not exist in the cell  $\underline{a} = 4.13$ ,  $\underline{c} = 8.49 \text{ \AA}$  because this contains only two  $\text{CO}_3$  groups, vertically arranged, <sup>the</sup> and with only two  $\text{CO}_3$  groups in/unit cell the structure can not accommodate a three-fold axis. McConnell (1960) found evidence for the real cell  $\underline{a}' = \sqrt{3}\underline{a}$ ,  $\underline{c}' = \underline{c}$ . Kahmi found  $\underline{a}' = \sqrt{3}\underline{a}$ ,  $\underline{c}' = 2\underline{c}$  (Table 14). Because most of the x-ray scattering is from the psuedo-cell, Kahmi analyzed the structure in terms of this cell in space group  $P6_3/\text{mmc}$  and gave positions for the carbon and oxygens in the  $\text{CO}_3$  group which are the result of averaging three orientations (Fig. 8). For Kahmi's structure  $R = 0.16$  which is about the limit of the data. Single crystals of vaterite good enough to extend Kahmi's averaged

Table 14

Pseudo-Cell and "True" Cell of Vaterite

Pseudo-Cell

"True" Cell (Kahmi)

a 4.13 Å

$\sqrt{3} \times 4.13 = 7.16 \text{ Å}$

c 8.49

$2 \times 8.49 = 16.98$

z 2

12

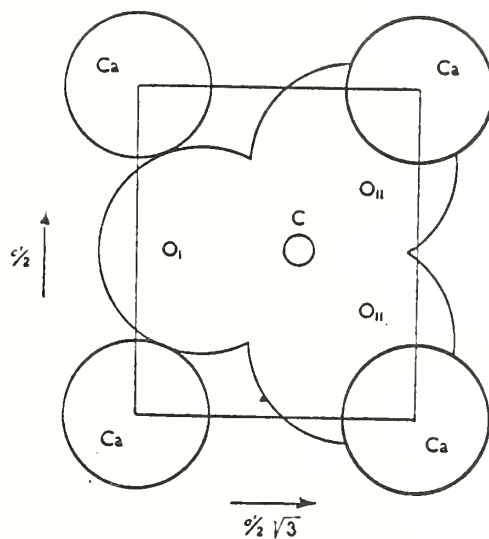
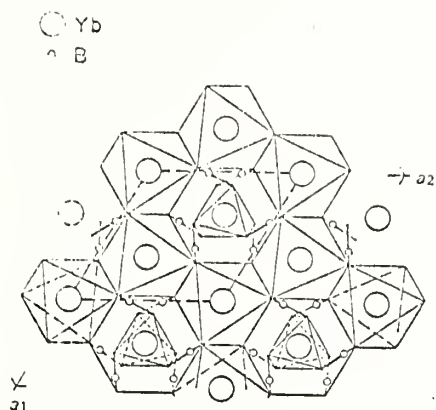


Figure 8. Kahmi's structure for the vaterite pseudo-cell. From Kahmi (1963).

structure into a three-dimensional structure have not yet been grown. Other routes to the vaterite structure may be through the structure of an isomorph or by lattice energy calculations on various models.

Various rare-earth borates apparently isostructural with vaterite have been studied (Battram and Felton, 1962; Newnham, Redman and Santoro, 1963; Bradley, Graf and Roth, 1966) and a structure for the high temperature form of  $\text{YbBO}_3$  has been suggested (Bradley, Graf and Roth, 1966) which is reported to be very close to Kahmi's for vaterite. Bradley, et al give  $x = .39$ ,  $y = .78$  for oxygen and Kahmi gives  $x = .38$ ,  $y = .76$ , all for the vaterite subcell. Bradley et al give the space group as probably being  $P6_322$  for their "real" cell  $a = 6.99$ ,  $c = 8.34 \text{ \AA}$ ,  $z = 6$ . Their suggested structure for the  $\text{YbBO}_3$  'isomorph' is given in Fig. 9. Since their cell is only half the vaterite cell along  $c$ , the structure of vaterite may consist of layers of the proposed  $\text{YbBO}_3$  structure displaced perpendicular to  $c$  to double the  $c$  translation.





The structure proposed by Bradley, Graf and Roth (1966) for the

Figure 9.

$\text{YbO}_3$ . This is a form of  $\underline{c}$ -axis projection of edge-sharing nets of  $\text{YbO}_6$  octahedra. The profiles of triangular borate ions above this net are indicated by heavy lines to the corners which they share with octahedra, and the positions of ions below the net by light lines.

(e)  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$

$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  may be an important compound in the nucleation of calcium carbonates in precipitation from aqueous solutions. It is the final form of calcium carbonate produced in an aqueous environment near  $0^\circ\text{C}$  in the presence of polyphosphates, (Brooks, Clark and Thurston, 1951). The  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  initially formed slowly redissolves with concomitant formation of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ .  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  crystallizes in the unit cell  $\underline{a} = 8.87 \pm .02 \text{ \AA}$ ,  $\underline{b} = 8.23 \pm .01 \text{ \AA}$ ,  $\underline{c} = 11.02 \pm .02 \text{ \AA}$ ,  $\beta = 110.2 \pm .1^\circ$  (at about  $-120^\circ\text{C}$ ) with space group  $\text{C}2/\text{c}$  and four formula weights per cell. The structure ( $R = 0.10$ , Figures 10 and 11) was determined (Dickens and Brown, 1968a) from photographic x-ray data collected from a crystal held at about  $-120^\circ\text{C}$ . It is of great interest because it contains discrete  $[\text{CaCO}_3]$  ion-pairs even though the structure contains enough water to coordinate Ca octahedrally. Each ion-pair is isolated from other ion-pairs by an envelope of 18 water molecules. Such ion-pairs may have a significant concentration in solutions saturated with respect to the calcium carbonates and may be important in mechanisms of biological transport. One factor preventing the formation of  $\text{Ca}(\text{OH}_2)_6$  "complexes" may be the difficulty in packing such complexes using only  $\text{CO}_3^{--}$  ions. However Ca does not have the affinity for water

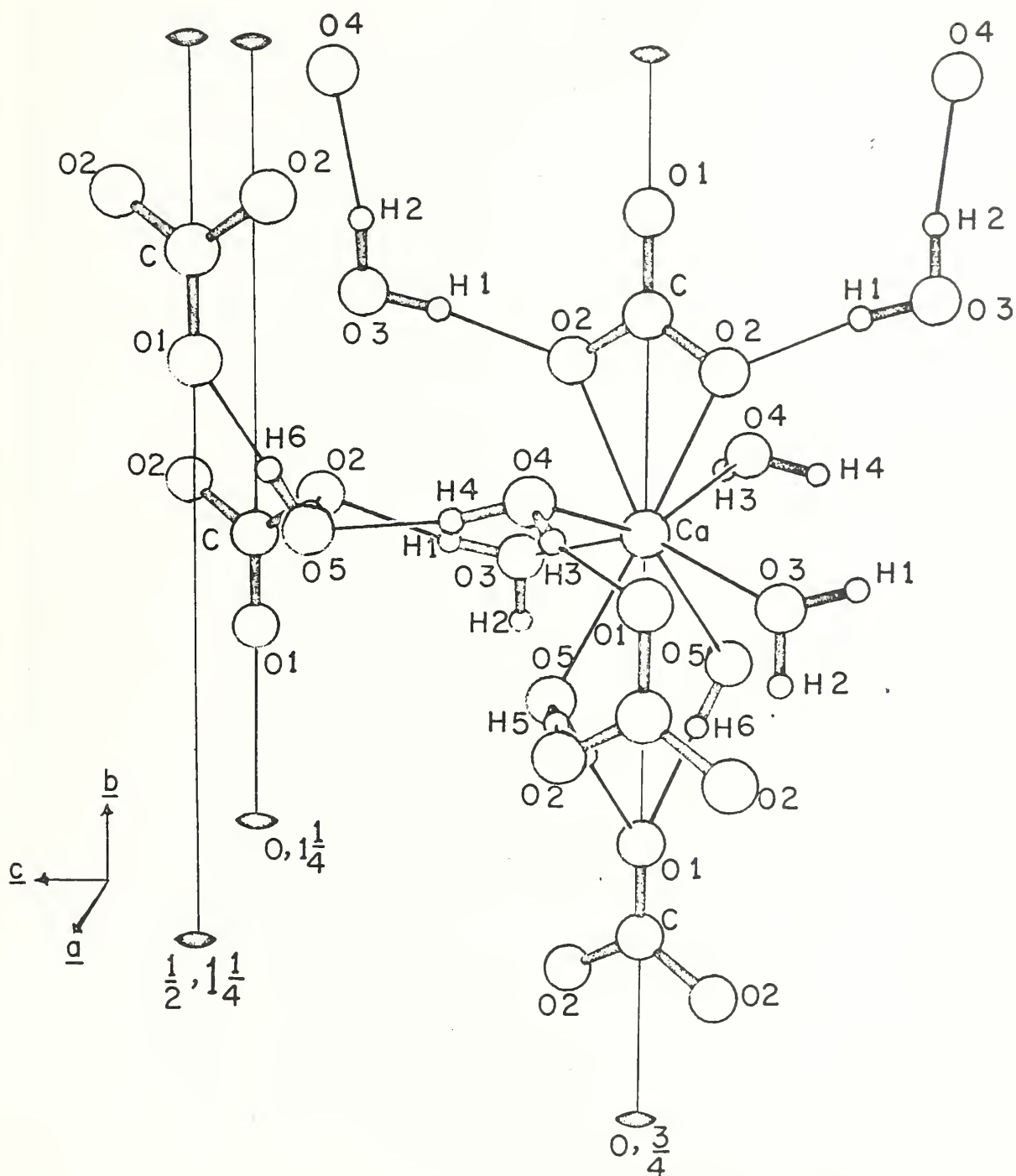


Figure 10. The  $\text{CaCO}_3$  ion-pair and the Ca ion environment in  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ . From Dickens and Brown (1968a).

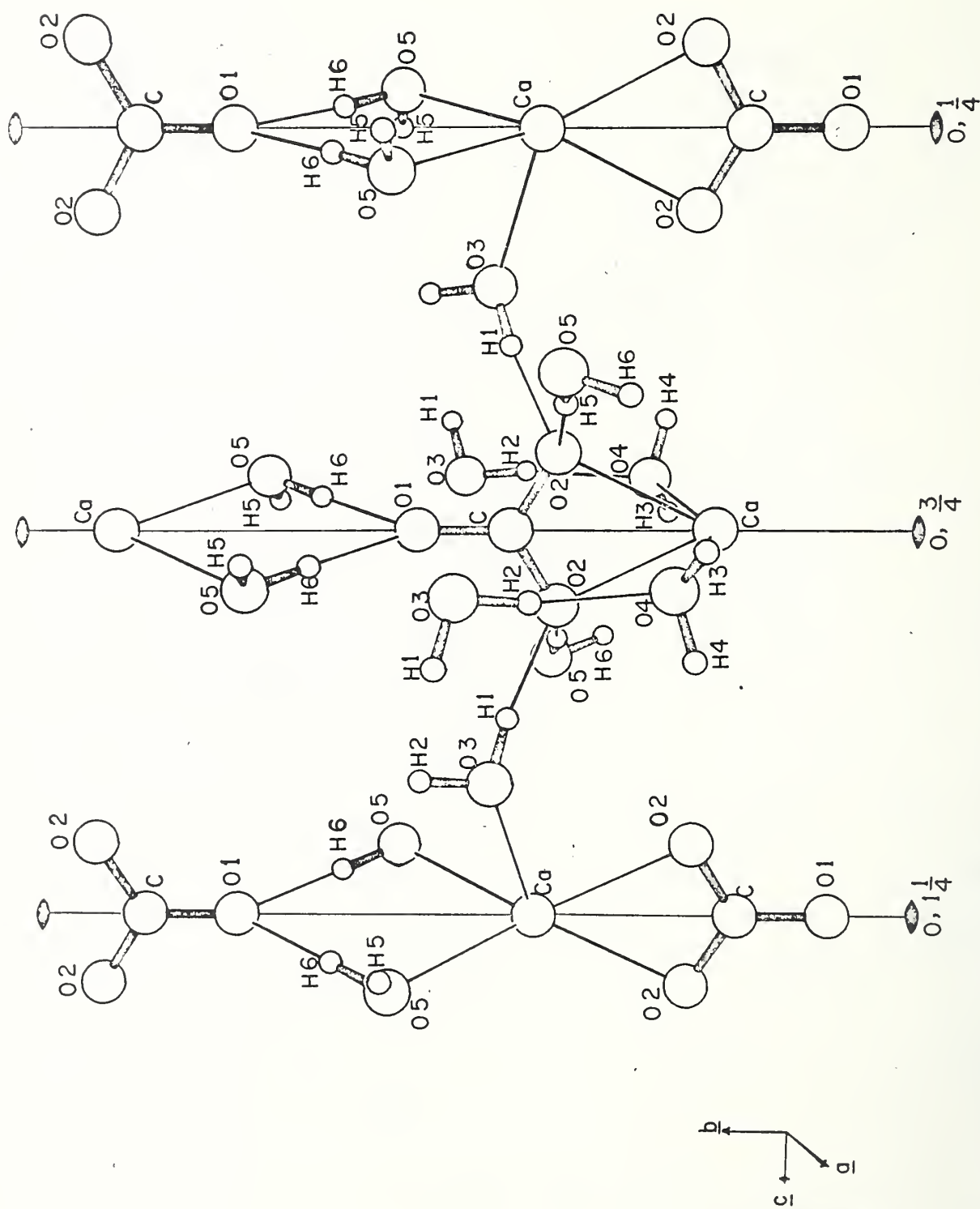
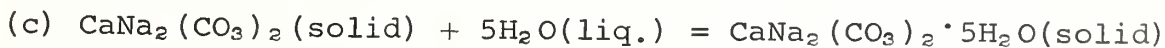
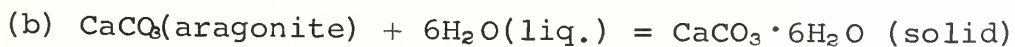
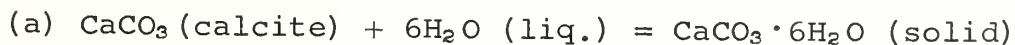


Figure 11. The  $\text{CaCO}_3$  pair and  $\text{CO}_3$  ion environments in  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ .

From Dickens and Brown (1968a).

of the increased importance, relative to the  $\text{Ca} \dots \text{O}$  term, of the  $\text{Ca} \dots \text{H}$  repulsion in the  $\text{Ca} \dots \text{OH}_2$  electrostatic compared with the corresponding terms in the interaction when  $\text{Mg} \dots \text{OH}_2$ . It is also noteworthy in this interaction respect that the highest stable hydrated Mg carbonate presently recognized is  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ , where Mg is probably coordinated to the five  $\text{H}_2\text{O}$  molecules and either a  $\text{CO}_3$  'apex' or 'edge'. Thus even Mg, with its many known instances of complete water coordination, may preferentially coordinate to  $\text{CO}_3^{=}$  in the presence of water molecules.

At atmospheric pressure, the reactions



would be accompanied by 20, 18 and 13 percent decreases in volume, respectively, suggesting that at high hydrostatic pressures (such as those that occur in the abyssal layer

of the oceans or in hydrostatic vessels)  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  in particular, and hydrated salts in general, may not only be present as nucleating particles for the reasons mentioned earlier, but may actually be the most stable forms. It is noteworthy in this connection that<sup>1)</sup> most deep sea animals have little or no calcareous materials in their skeletons (Svendrup, Johnson and Fleming, 1942) suggesting that anhydrous calcium carbonates are not easily formed at these depths,<sup>2)</sup> and that  $\text{CaCO}_3$  is essentially absent from sediments collected at depths greater than 5,000 m (Arrhenius, 1963) and Laughton, presumably because of its increased solubility (Heezen /1963). It has been suggested (Riedel, 1963) from an electron microscopic examination that almost all the calcium carbonate in deep sea sediments is of organic origin and has not been changed by recrystallization after deposition. However, the possibility must be considered that at great depths the calcium carbonates in such sediments can be converted in part into hydrated forms which prevent the formation of normal skeletons and which rapidly decompose to the anhydrous forms at normal temperatures and pressures (.i.e., during sample recovery).

(f)  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$

$\text{CaCO}_3 \cdot \text{H}_2\text{O}$  usually has a spherulitic habit (Brooks, Clark and Thurston, 1951) and its structure is unknown at present. It is the first macroscopic phase obtained in the preparation of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$  (gaylussite) by precipitation from aqueous solution in gel form in the presence of polyphosphates.  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  has been grown as single crystals by Lippmann (1959) by hydrolysing KCNO in aqueous solution with  $\text{MgCl}_2$  and  $\text{CaCl}_2$  in a closed vessel at  $20^\circ\text{C}$ . The structure has a pronounced pseudo-cell (Table 15).  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  is of considerable interest since it is so readily produced (in spherulitic form) in the presence of crystal growth poisons which inhibit the formation of calcite. It is stable for several months at  $20^\circ\text{C}$  in air.

(g) Gaylussite  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$

Gaylussite is found as a mineral and in the solid phase eventually formed/at room temperature from aqueous solution when a large excess of  $\text{Na}_2\text{CO}_3$  solution is added to  $\text{CaCl}_2$  solution in the presence of polyphosphate. The unit cell has dimensions  $\underline{a} = 14.361(2) \text{ \AA}$ ,  $\underline{b} = 7.781(4) \text{ \AA}$ ,  $\underline{c} = 11.209(2) \text{ \AA}$  and  $\beta = 127.84(1)^\circ$ , with space group  $\text{C2/c}$ . The structure has been determined (Dickens and Brown, 1968 b), ( $R_w = 0.043$ ),

Table 15

The "True" and Pseudo Cells of  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$

$\underline{a}$       10.62 Å      pseudo cell  $\underline{a}' = 6.13$  Å

$\underline{c}$       7.54       $\underline{c} = 7.61$

$z$       9      2

$a = \sqrt{3}a'$

space-group  $D_3^{(4,6)} P3,21$  or  $D_3^{(3,5)} P3,21$

density 2.38 g/ml



and the hydrogen atoms have been located approximately. Specific details are shown in Fig. 12 and 13. The structure contains  $\text{CO}_3\text{-Ca-CO}_3$  ion triplets isolated from each other but coordinated to Na ions and water molecules. These triplets could be of importance in biological transport. The structure is more fully discussed by Dickens and Brown (1968b).

(h) Pirssonite,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$

Pirssonite is found as a mineral and is the solid phase formed instead of gaylussite when the reactants are maintained at  $50^\circ\text{C}$ . The cell data are given in Table 16. Its structure has been determined from natural (Corazza and Sabelli, 1967) and synthetic (Dickens and Brown, 1968 b) material. For the latter determination  $R_w = 0.029$ . Despite the resemblance of its cell dimensions to those of  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , trona, it is not structurally related. The structure (Fig. 14, 15) contains ion triplets (Fig. 14) very much like those in gaylussite except that the triplets are further coordinated together (Fig. 14, 15) because there are not enough water molecules in the structure to complete the

Table 16

Cell Data for Pirssonite

Evans	Dickens and Brown (1968)
<u>a</u> = 11.32	11.340(4)
<u>b</u> = 20.06	20.096(5)
<u>c</u> = 6.00 Å	6.034(2)
Space group Fdd2	
z = 8	
density = 2.367 g/ml	

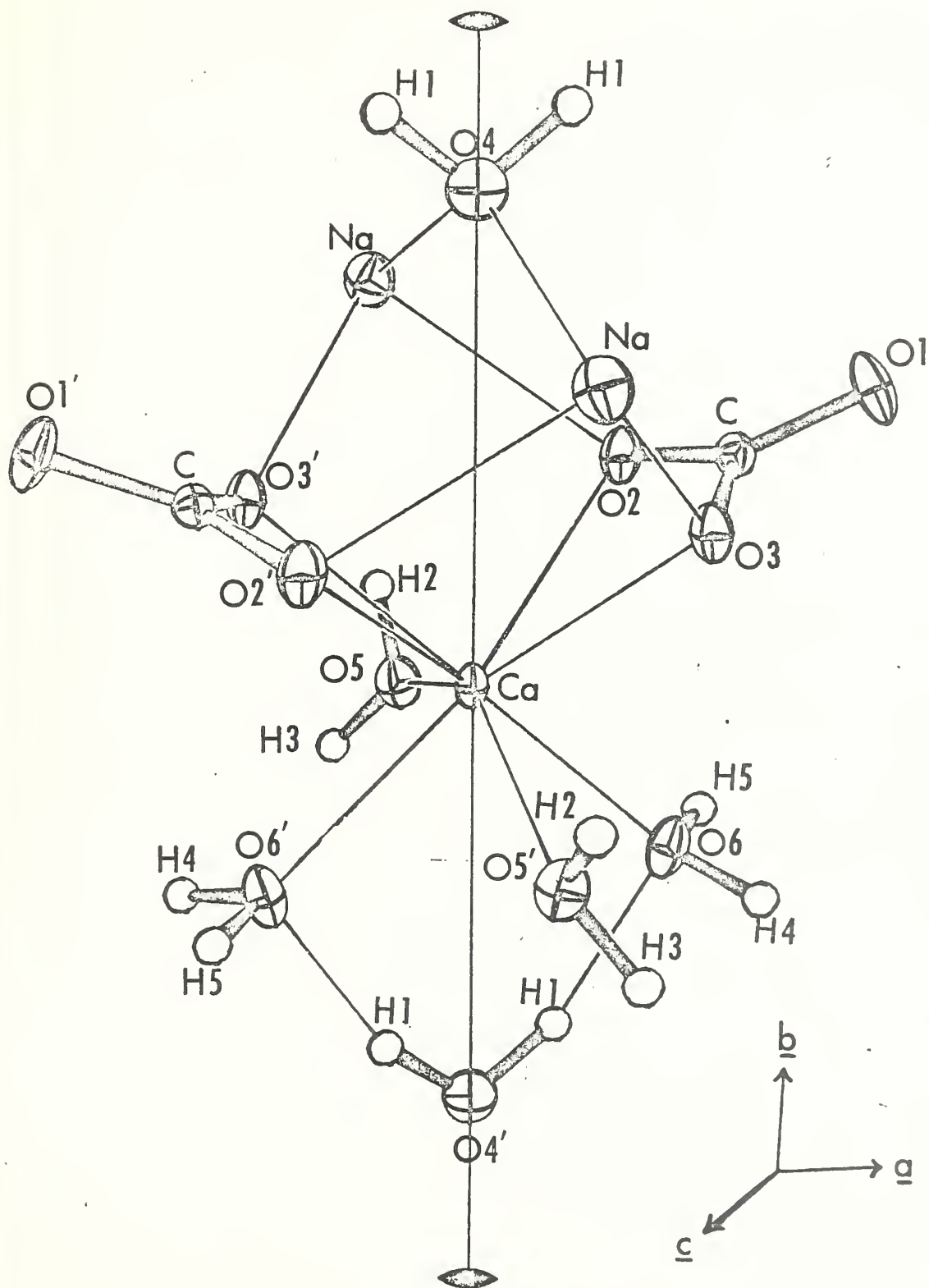


Figure 12. The  $\text{CO}_3\text{CaCO}_3$  triplet and the Ca environment in  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$  (gaylussite). From Dickens and Brown (1968b).

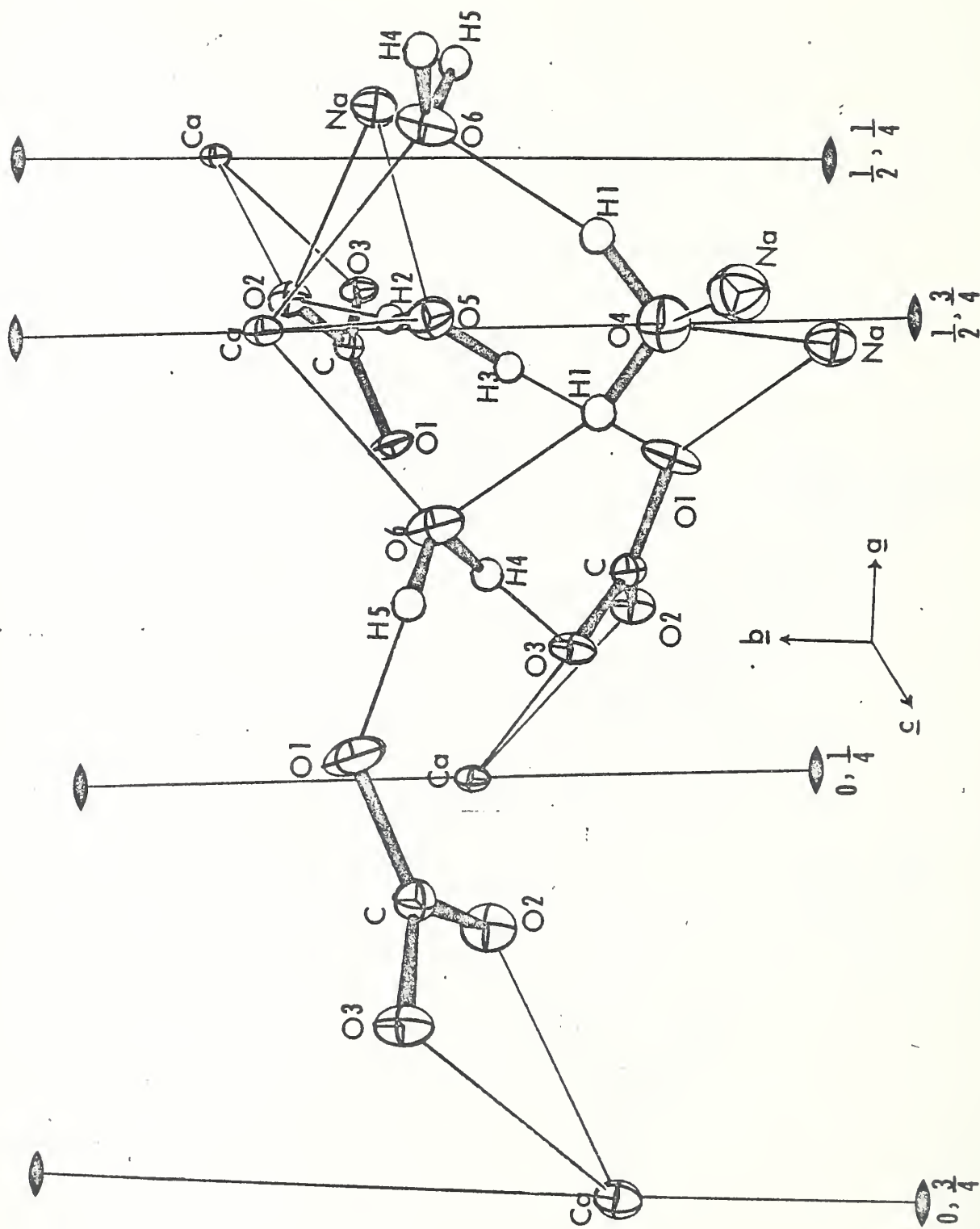


Figure 13. The hydrogen bonding in  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$  (gaylussite). From Dickens and Brown, (1968b).

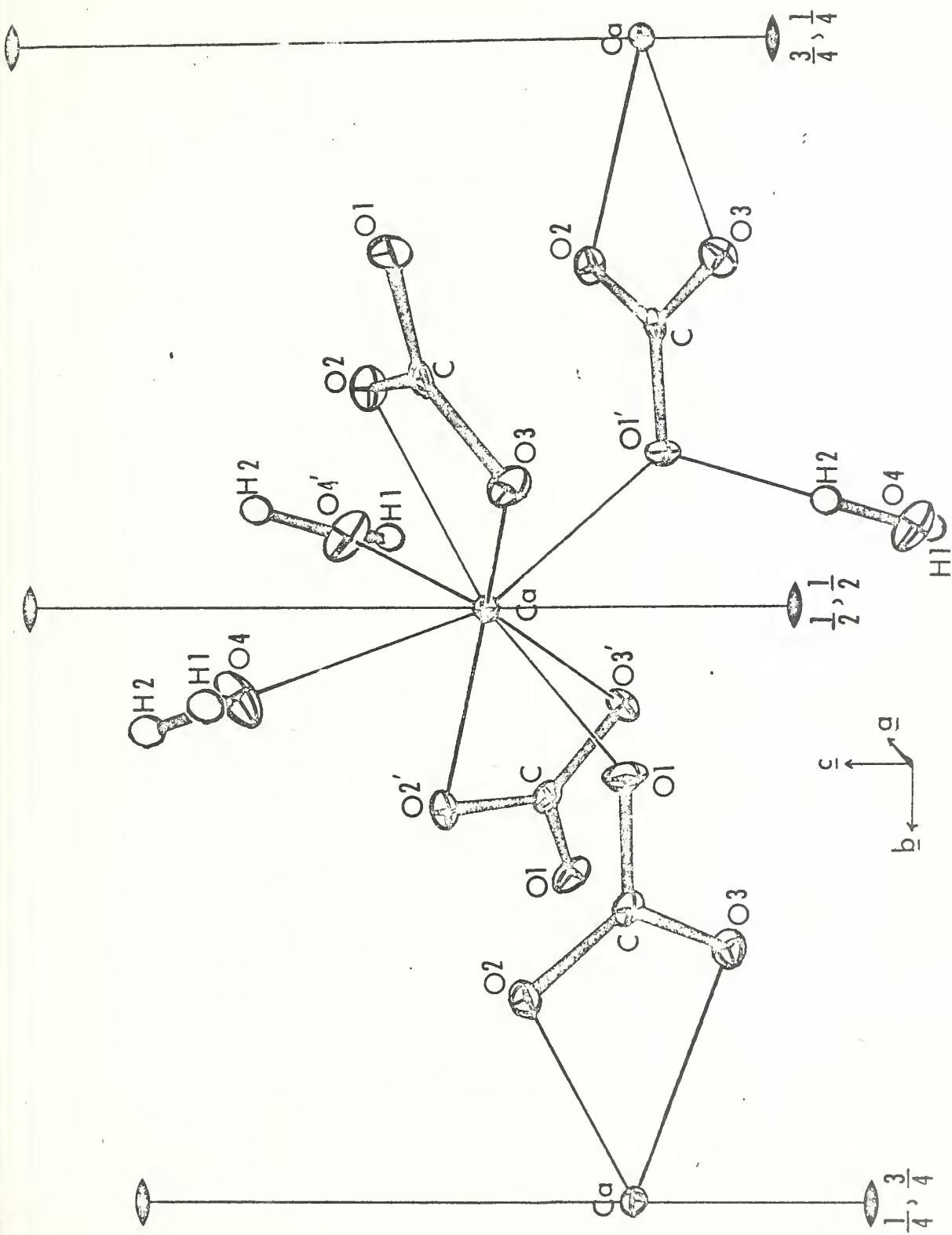


Figure 14. The  $\text{CO}_3\text{CaCO}_3$  triplets in  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$  (pirssonite). From Dickens and Brown (1968b).

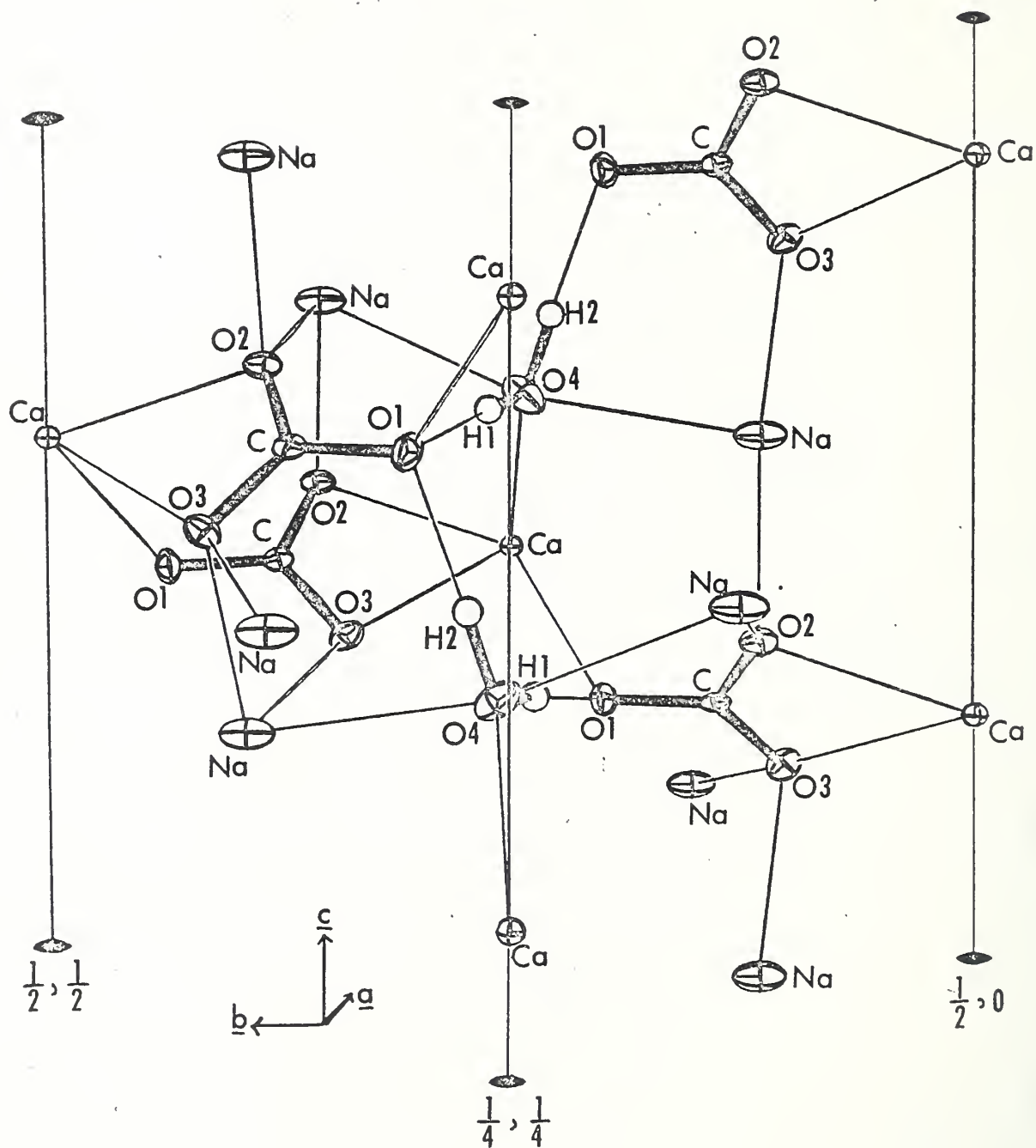


Figure 15. The detailed bonding in  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$  (pirssonite). From Dickens and Brown (1968b).

coordination round the Ca ions. Other features of the coordination are shown in Fig. 14 and 15. The structure is more fully discussed by Dickens and Brown (1968b).

Pirssonite may be important in the otoliths of benthic fishes which are found (Morris and Kittleman, 1967) to be well stratified into distinct species in the sea. The otoliths are strongly piezo-electric and it has been suggested that this may be the mechanism by which the fishes perceive their depth, since they do not have gas bladders. The major inorganic component of the otoliths is aragonite, which, being centrosymmetric, cannot be piezo-electric. Pirssonite, however, is non-centrosymmetric and consists of ions commonly present in sea water, although it is not normally formed under conditions expected in sea water (Bury and Redd, 1933). Organic components in the otoliths also may be responsible for the piezo-electricity, however, as has been suggested for bone (Shamos / ). Other possible candidates are shortite and  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . Using a crude apparatus we have found both pirssonite and shortite to exhibit piezo-electricity. Our sample of small plates of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  did not give a positive test under these conditions, although Harper (1936) observed such an effect.

(i) Shortite  $\text{Ca}_2\text{Na}_2(\text{CO}_3)_3$

Shortite is found mainly as a mineral and, because it is non-centrosymmetric, may, like pirssonite, be of importance in generating the piezo-electricity of some otoliths. Its structure has been determined (Wickman, 1949) but there are some large discrepancies between the calculated and the qualitatively observed structure factors and the structure needs refining.



### 3. OTHER STRUCTURES OF INTEREST

#### (a) Brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

Brushite was first found in 1865 by G. E. Moore (1865) in druses in phosphate rock from Avis Island in the Caribbean Sea. It frequently occurs as encrustations on ancient human and animal bones (Fronzel, 1943) and is found in human urinary calculi (Lonsdale, Sutor and Wooley, 1968). The structure is related to that of gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Atoji and Rundle, 1958), and was first refined (Beevers, 1958) in the same centrosymmetric space group  $I2/a$ . Chemical considerations and the observance of a pronounced piezoelectric effect prompted refinement to ( $R = 0.164$ ) in the non-centrosymmetric space group  $Ia$  (Jones and Smith, 1962). The refinement used Beever's original data which was uncorrected for what must have been appreciable absorption. More recent work (Jones, 1968) using an incomplete set of neutron data collected from a large single crystal of brushite retains the overall structural similarity of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , including the hydrogen bonding of the water molecules, although the detailed atomic distances in the two cases are different. The 'acid' hydrogen in  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , which presumably distorts the space group from  $I2/a$  to  $I/a$ , is suggested to be located between  $0(1)$  and  $0(4')$  (Jones, 1968), i.e., in the  $\text{CaPO}_4$  layer. The positions

of the heavy atoms have not yet been refined from those in Jones and Smith (1962). Further refinement with new data is necessary. The structure (Figure 16) consists of  $\text{CaPO}_4$  sheets like those which have been found in several other calcium phosphate structures (in gypsum there are similar  $\text{CaSO}_4$  sheets). The sheets consist of neighboring chains of alternating Ca and  $\text{PO}_4$  ions and are linked together by interleaved layers of water molecules. The water molecules hydrogen bond to the oxygens of the  $\text{PO}_4$  ions on the surfaces of the  $\text{CaPO}_4$  sheets and are electrostatically bonded to the Ca's. The structure may be rationalized from Figure 17 which is the monetite ( $\text{CaHPO}_4$ ) structure idealized into a tetragonal structure. Figure 17 is also essentially Hohne, 1962; the anhydrite ( $\text{CaSO}_4$ ) structure (Cheng and Zussman, 1963).

In  $\text{CaSO}_4$ , the structure is orthorhombic with  $a = 6.991$ ,  $b = 6.996$ ,  $c = 6.238$  (Swanson, Fugat and Ugrinic, 1955). If A is a central Ca/ $\text{PO}_4$  in  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  B and C are

$\text{CaHPO}_4$  chains and D and E are water molecules.

Similarly, in  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  the Ca's in the B and C chains are coordinated to water molecules on the side away from the A chain so that the layer in both brushite and gypsum is a zigzag interlocking of chains. In brushite, presumably there is distortion of the chain by the hydrogen bonding between  $\text{PO}_4$  groups.

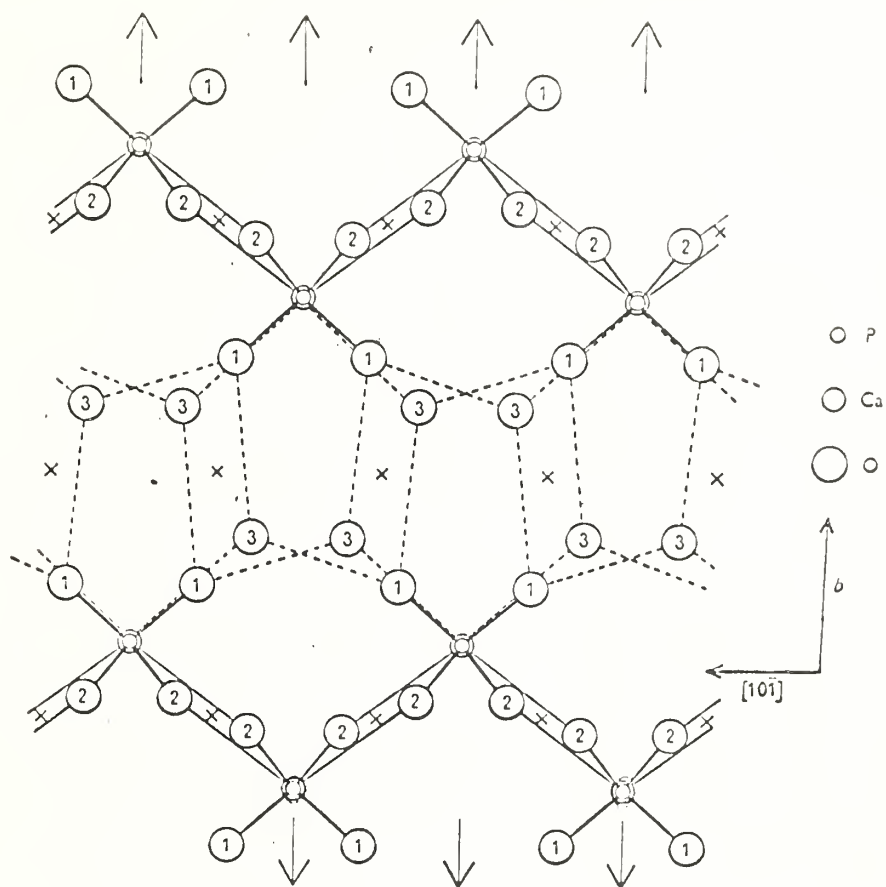


Figure 16. Projection of the structure of brushite on to a plane perpendicular to  $[101]$ . From Beevers (1958).

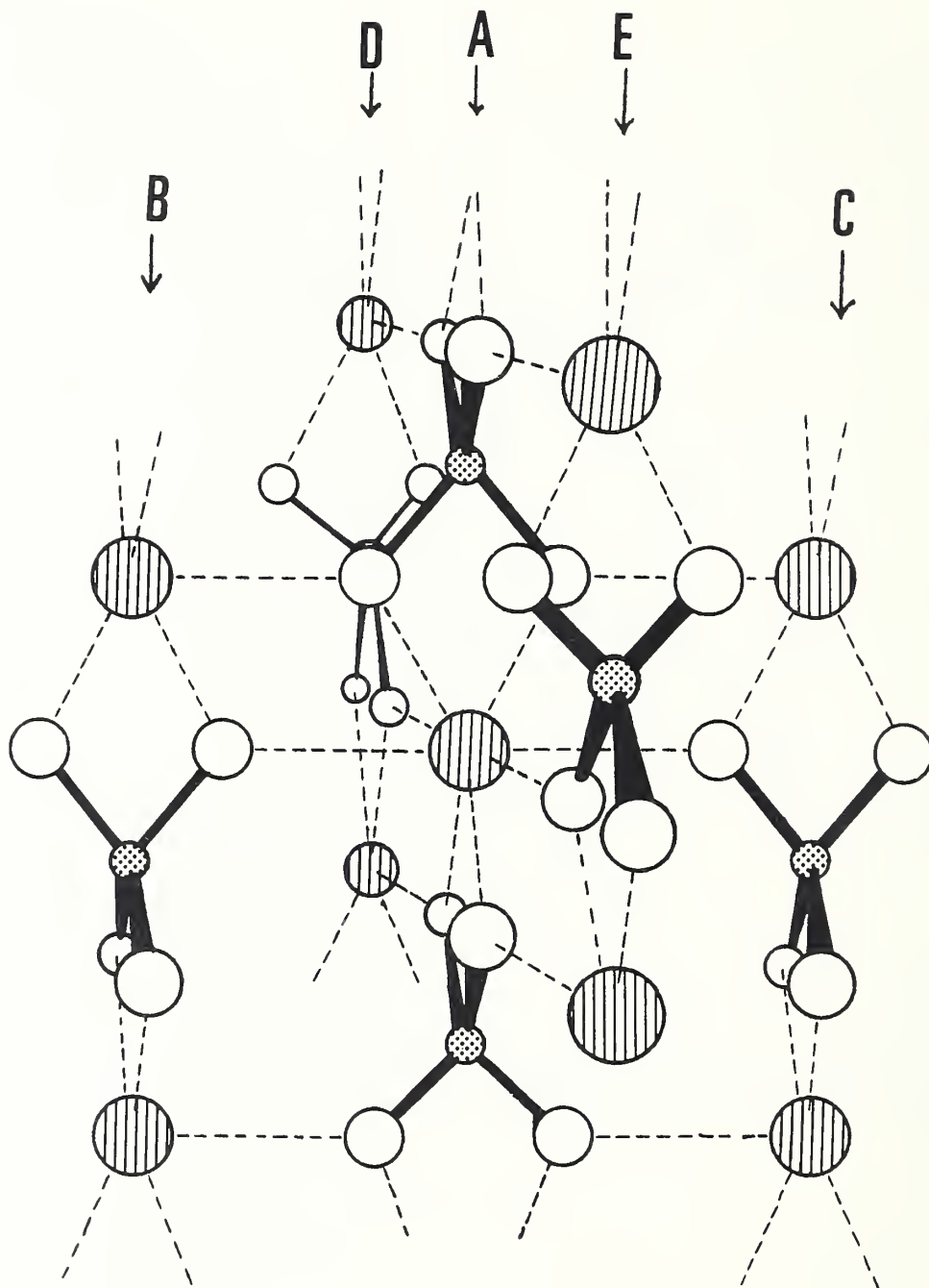
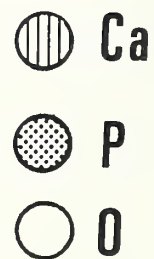


Figure 17. An idealized tetragonal  $\text{Ca}(\text{H})\text{PO}_4$  structure.



(b) Monetite  $\text{CaHPO}_4$

The crystal structure of monetite has been determined (MacLennan and Beevers, 1955; Jones and Cruickshank, 1961) with moderate precision ( $R = 0.15$ ) from photographic x-ray data uncorrected for what must have been appreciable absorption. The hydrogen positions have been determined (Curry, Denne and Jones, 1968) using neutron data and are consistent with observed P-O lengths and NMR data. The heavy atom positions have not been refined from the positions reported in Jones and Cruickshank (1961). Further work (Curry, Denne and Jones, 1968) is continuing on monetite.

The structure (Figure B) contains sheets of  $\text{CaHPO}_4$  which are bonded to one another by  $\text{Ca}\dots\text{O}$  electrostatic bonds and by hydrogen bonds. The shortest  $\text{O}\dots\text{O}$  distance in the structure is  $\text{O}(7)\dots\text{O}(7') = 2.44 \pm .03 \text{ \AA}$  across the center of symmetry. The hydrogen is disordered about this center of symmetry so that the bond contains half a hydrogen on average on each side of the center. The remaining "half" hydrogen is similarly disordered in the  $\text{O}(1)\dots\text{O}(5)$  region, where the

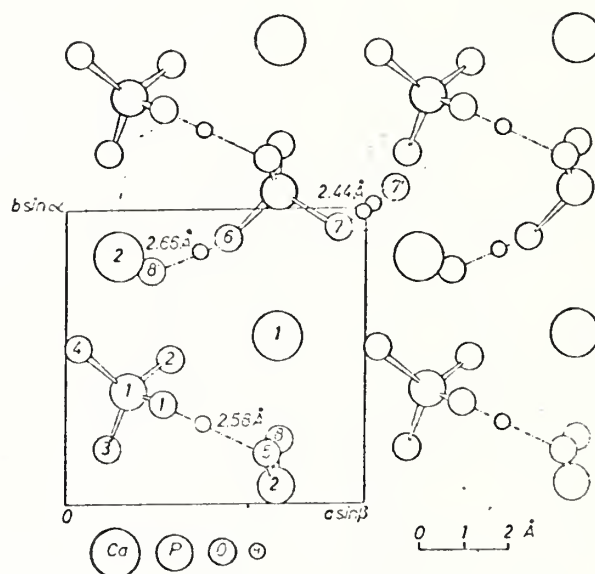


Figure 18. Monetite: projection of one layer of the crystal structure on to the plane perpendicular to [001]; the other layer (of which only  $O_7'$  and  $O_8'$  is shown) is related to this by a center of symmetry. The smallest circles represent probable hydrogen sites.

From Jones and Cruickshank (1961).

interatomic distance is  $2.58 \pm .02 \text{ \AA}$ . The remaining hydrogen in the unit cell is on O(6) and forms an essentially linear hydrogen bond to O(8) with  $O(6) \dots O(8) = 2.66 \pm .02 \text{ \AA}$ . The structure of monetite is essentially the structure given in Figure 17 distorted to triclinic by the hydrogen bonding and perhaps by the lack of fit of the O 'cage' and the Ca ionic radius.



The structure of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (Figures 19, 20) has been determined (MacLennan and Beevers, 1956; Jones and Cruickshank, 1961) with moderate precision ( $R = 0.16$ ) from photographic x-ray data uncorrected for absorption. The hydrogens have been placed (Jones and Cruickshank, 1961) provisionally from considerations of the P-O bond lengths in the  $\text{PO}_4$  group and of  $O \dots O$  distances in the structure. In the P(1)  $\text{PO}_4$  group, two statistically disordered hydrogens have been suggested, from O(1) to O(1') ( $2.67 \pm .05 \text{ \AA}$ ) across the center of symmetry and (a little less likely) from O(4) to O(9) ( $O(4) \dots O(9) = 2.60 \pm .03 \text{ \AA}$ ). O(3) is assigned a hydrogen which is hydrogen bonded to O(5) ( $O(3) \dots O(5) = 2.48 \pm .03 \text{ \AA}$ ). In the P(2)  $\text{PO}_4$  group, the P-O distances suggest the assignment of one hydrogen to O(6), forming a hydrogen bond to O(8) ( $O(6) \dots O(8) = 2.72 \pm .04 \text{ \AA}$ ), and one hydrogen

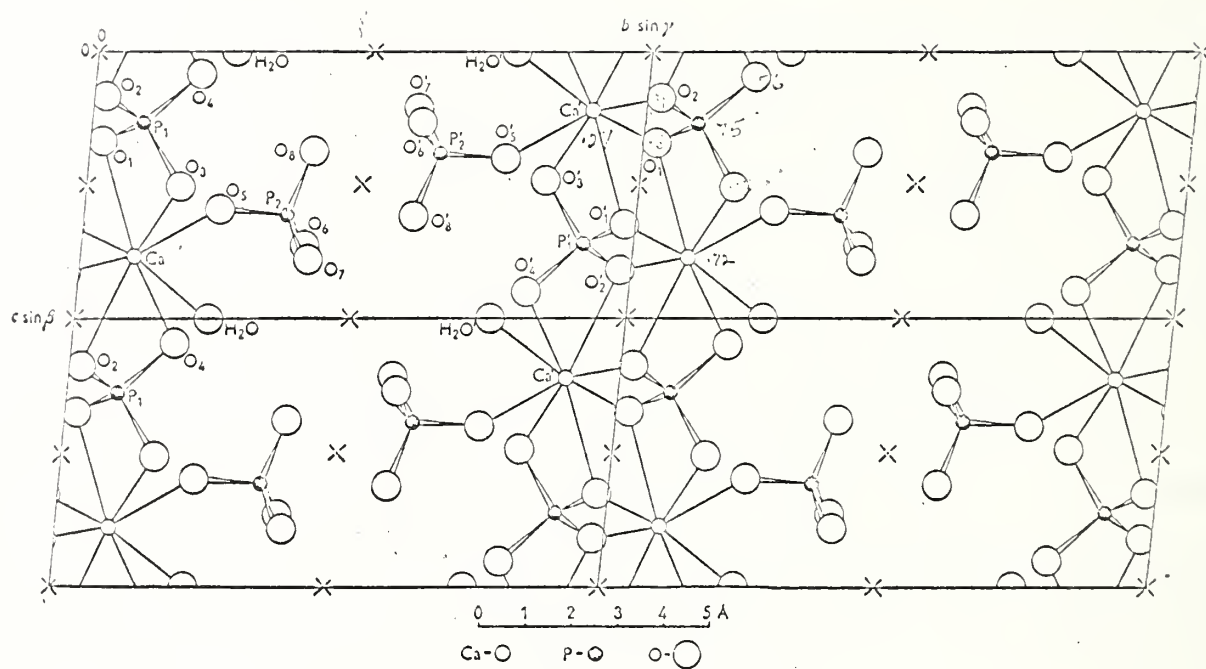


Figure 19. Four unit cells of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , projected down the a axis. From MacLennan and Beevers (1956).



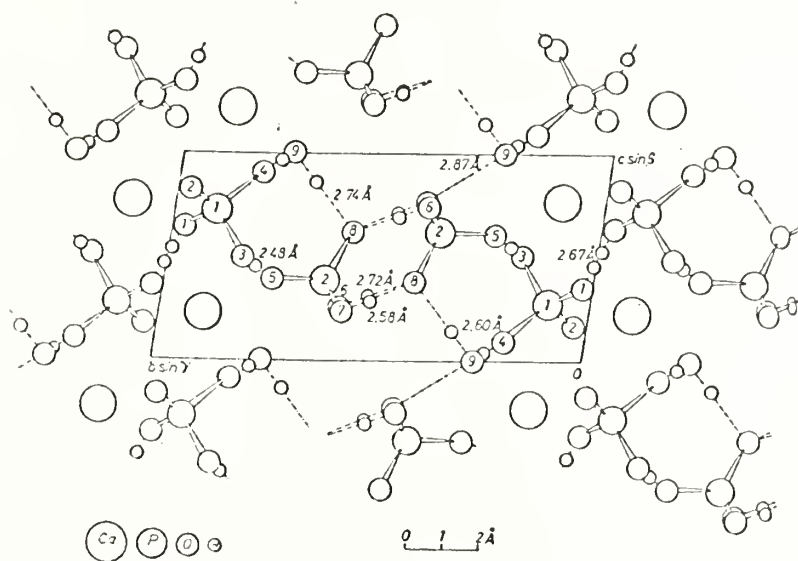


Figure 20. Projection of the crystal structure of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  onto the plane perpendicular to  $[100]$ .  
From Jones and Cruickshank (1961).

to O(7), forming a hydrogen bond to O(8) ( $O(7) \dots O(8) = 2.58 \pm .04 \text{ \AA}$ ). The hydrogens of the water molecules hydrogen bond to O(4) ( $O(9) \dots O(4) = 2.60 \pm .03 \text{ \AA}$ ) and to O(8) ( $O(9) \dots O(8) = 2.74 \pm .03 \text{ \AA}$ ). Neutron data on a twinned crystal of  $Ca(H_2PO_4)_2 \cdot H_2O$  are being collected (Curry, Denne and Jones, 1968). The  $CaPO_4$  layer structure for  $Ca(HPO_4)_2 \cdot H_2O$  is very similar to that for  $CaHPO_4 \cdot 2H_2O$ , if the hydrogen atoms are ignored. One of the water molecules, say position <sup>E</sup> in Figure 17, in  $CaHPO_4 \cdot 2H_2O$  is the oxygen O(5) of a  $PO_4$  group which is hydrogen bonded to its centro-symmetrically related partner (Figures 19,20). Successive sheets in  $Ca(H_2PO_4)_2 \cdot 2H_2O$  crystallographically are not/related by a rotation about  $180^\circ$  as they are in gypsum and brushite and the occasional crystallization of layers rotated by  $180^\circ$  explains the observed twinning of  $Ca(H_2PO_4)_2 \cdot H_2O$ . The fact that there are similar (MacLennan and Beevers, 1956). /sheets in the above compounds account for their observed intergrowths (Lehr, Smith and Brown, 1952).

The structure of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is also related (Brown, Smith, Lehr and Frazier, 1958) to several other calcium phosphate compounds as shown in Table 17.

(d)  $\text{Ca}_2\text{PO}_4\text{Cl}$  chlorospodiosite

The crystal structures of  $\text{Ca}_2\text{PO}_4\text{Cl}$  (Figure 21) and its analog  $\text{Ca}_2\text{CrO}_4\text{Cl}$  have recently been determined (Greenblatt, Banks and Post, 1967) with  $R = 0.043$  and  $0.041$ , respectively. The structure of  $\text{Ca}_2\text{PO}_4\text{Cl}$  contains  $\text{CaPO}_4$  layers which are easily constructed from Figure 17 by taking a planar sheet consisting of the ABC chains and replacing those oxygens in chains D and E which are coordinated to the Ca in the A chain/ by  $\text{Cl}^-$  ions. The  $\text{Cl}$  ions are in turn coordinated to another planar sheet on thier far side. The voids left between adjacent  $\text{CaPO}_4$  sheets and in the  $\text{Cl}^-$  layer are filled by Ca ions. The whole structure undergoes some slight rearrangement, seemingly based on the second type of Ca being coordinated most efficiently to the two  $\text{PO}_4$  edges in the six oxygen atoms in its coordination environment. The other two oxygens in this environment are  $\text{PO}_4$  apices. These six oxygens form a cyclo-hexane shaped boat with the Ca just above the 'deck' and with two Cl ions at right angles to the prow-stern line completing the Ca coordination as a 'sail'. The oxygen 'boats' share a common side and adjacent ones are inverted. The  $\text{CaPO}_4$  chains, apart from being

Table 17

The Unit Cell Data of Several Compounds Related to  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ 

	$\text{Ca}_2(\text{NH}_4)_2\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	$\text{Ca}_2(\text{K})\text{H}_7\text{PO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Ca}_2\text{H}_8(\text{PO}_4) \cdot 2\text{H}_2\text{O}$	$\text{CaCl}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
<u>a</u>	5.79 Å	5.72 Å	5.67 Å	5.76 Å
<u>b</u>	12.52	12.13	11.92	17.14
<u>c</u>	6.50	6.46	6.51	6.41
$\alpha$	97°57'	98°44'	98°11'	90°
$\beta$	117°45'	118°1'	118°31'	119°
$\gamma$	98°0'	95°54'	83°9'	90°
density	5.99	5.90	5.89	8.57
FW/cell	1	1	2	4

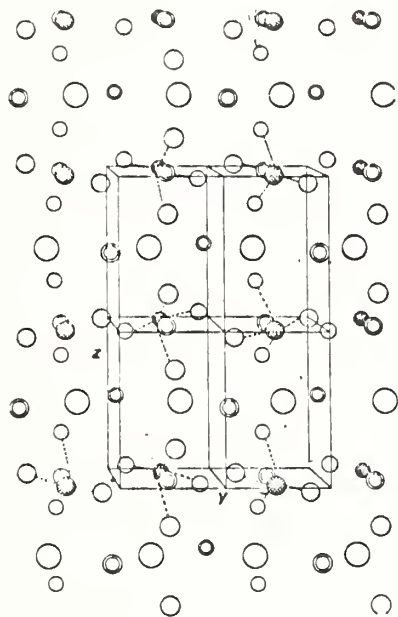
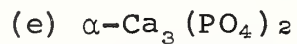


Figure 21. The unit-cell contents of  $\text{Ca}_2\text{PO}_4\text{Cl}$  viewed along  $\underline{a}$ . Large open circles, Cl; atoms shaded up and down, P; double circles, Ca; smaller open circles, O. Bonds between the atoms in  $\text{PO}_4^{3-}$  tetrahedra are represented by broken lines. From Greenblatt, Banks and Post (1967).

slightly rotated about their axis by coordination to interlayer Ca ions, are regular because no hydrogens are present to distort them through hydrogen bonding.



$\alpha\text{-Ca}_3(\text{PO}_4)_2$  is the form of  $\text{Ca}_3(\text{PO}_4)_2$  stable above  $1180^\circ\text{C}$ . MacKay (1953) assigned to it the monoclinic cell  $\underline{a} = 12.86 \pm .02$ ,  $\underline{b} = 9.11 \pm .01$ ,  $\underline{c} = 15.23 \pm .02$ ,  $\beta = 125.3 \pm .2^\circ$  and the space group  $\text{P}2_1/a$  with  $z = 8$ . A pseudo-orthorhombic cell  $\underline{a} = 15.22$ ,  $\underline{b} = 20.71$ ,  $\underline{c} = 9.109 \text{ \AA}$  has been reported (DeWolff). MacKay noted considerable hexagonal pseudo-symmetry in the  $hk0$  layer of the reciprocal lattice, i.e., in the projection of the structure along  $\underline{c}$ . In three dimensions the structure is not pseudo-hexagonal. From two-dimensional Patterson syntheses he suggested the structure contained 12 columns of Ca and  $\text{PO}_4$  ions parallel to  $\underline{c}$ , the columns being spaced about  $3 \text{ \AA}$  apart with the heavy atoms Ca and P about  $3.8 \text{ \AA}$  apart in the columns. More recently, Epstein (1968) has found that the  $\underline{b}$  axis is invariably tripled in samples he has examined, and we have confirmed this. He found trial positions for the heavy atoms but could not find positions for the light atoms which would allow the structure to refine. He considered two structures with packings similar to the chains of Ca and  $\text{PO}_4$  ions in structures such as  $\text{CaHPO}_4$ .

(f)  $\beta\text{Ca}_3(\text{PO}_4)_2$

$\beta\text{Ca}_2(\text{PO}_4)_2$  is the form of  $\text{Ca}_3(\text{PO}_4)_2$  stable at temperatures below  $1180^\circ$  and is trigonal (Fron del 1941, 1943; Mac ay, 1952) with  $\underline{a} = 10.32 \text{ \AA}$ ,  $\underline{c} = 37.0 \text{ \AA}$ , space group  $\text{R}\bar{3}\text{c}$  and  $z = 7$ . It exists as the mineral whitlockite and is often a pathological calcified deposit in the body. There is an anomaly in that 21 Ca's (in 7 formula weights of  $\text{Ca}_3(\text{PO}_4)_2$ ) cannot fit in space group  $\text{R}\bar{3}\text{c}$  without statistical disordering. Brown and Wallace have recently (1968) shown by heating mixtures of  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  to form  $\beta\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ca}_4\text{P}_2\text{O}_7$  and subsequently analyzing for  $\text{P}_2\text{O}_7^{4-}$  that the ratio of Ca/P in  $\beta\text{Ca}_3(\text{PO}_4)_2$  is 21/14 and not 20/14 (which would fit in space group  $\text{R}\bar{3}\text{c}$ ). The structure of  $\beta\text{Ca}_3(\text{PO}_4)_2$  is not yet known.

(g)  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$

The structure of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  has recently been determined by Dickens and Brown to the point of final refinement ( $R = 0.08$ ). The formula is really  $\text{Ca}_{3.5}\text{Mg}_{4.5}(\text{Ca, Mg})(\text{PO}_4)_6$ . Ca and Mg are present in the variable site in about equal amounts in our crystal, making the empirical formula  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ . When the structure is reviewed along [201] an approximate  $\bar{3}$

axis can be discerned if small shifts in the atomic positions and the difference between Ca and Mg are ignored. A pseudo-hexagonal cell  $\underline{a}' = 6.86 \text{ \AA}$ ,  $\underline{b}' = 9.99$  and  $\underline{c}' = 14.88 \text{ \AA}$  can be defined. Similarities between this cell and that of  $\text{NaK}_3(\text{SO}_4)_2$  (glaserite) can be seen. As in glaserite, there are cation columns and cation-anion columns in  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ . The cation-anion columns in  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  have every other cation site vacant.

One of the main objectives in our study of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  is to find relationships between it and the two better known tricalcium phosphates,  $\beta\text{-Ca}_3(\text{PO}_4)_2$ , and  $\alpha\text{-Ca}_3(\text{PO}_4)_2$ , neither of which has a known structure. The dimensions of the pseudo-orthohexagonal cell of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  strongly suggest that there are relationships between it and the two tricalcium phosphates. For example, whitlockite is known to have a prominent repeat of  $\underline{c}/10$  (i.e.,  $3.74 \text{ \AA}$ ) in its cell structure. The pseudo-orthohexagonal described above has a similar repeat of  $\underline{c}'/4$  (i.e.,  $3.72 \text{ \AA}$ ). The  $\underline{a}$  axis of whitlockite,  $10.43 \text{ \AA}$ , is quite similar to  $\underline{b}'$  of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ ,  $9.99 \text{ \AA}$ . The dimensions of the pseudo-orthorhombic cell of  $\alpha\text{-Ca}_3(\text{PO}_4)_2$ ,  $\underline{a} = 15.23$ ,  $\underline{b} = 20.71$



and  $\underline{c} = 9.11 \text{ \AA}$ , are also similar to those of the pseudo-orthohexagonal cell of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ . It now appears that no two of these compounds are isostructural, but it is likely that they will share important structural features. The unit cell and related data of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  are compared with those of  $\alpha\text{Ca}_3(\text{PO}_4)_2$ ,  $\beta\text{Ca}_2(\text{PO}_4)_2$  and  $\text{NaK}_3(\text{SO}_4)_2$  (glaserite) in Table 18.

#### (h) Calcium Oxalates

Other important constituents of human urinary calculi are the compounds  $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$  (whewellite) and  $\text{Ca}(\text{COO})_2 \cdot 2 \cdot 2\text{H}_2\text{O}$  (weddellite), which are also found as minerals. The structures of both have been determined. Whewellite is monoclinic,  $\underline{a} = 6.24$ ,  $\underline{b} = 14.58$ ,  $\underline{c} = 9.89$ ,  $\beta = 107^\circ$ ,  $z = 8$  with space group  $\text{P}2_1/\text{c}$ ,  $R = .13-.15$ . Its structure (Cocco and Carobbi, 1961; Cocco and Sabelli, 1962) is shown in Figure 22. The Ca's are coordinated by the longer edge of the oxalate anion, which presumably allows each oxygen to coordinate to two Ca's more easily. Apparently the hydrogen atoms were not located.

Table 18

A Comparison of the Unit Cell Data of

$\alpha$  and  $\beta\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  and

$\text{Na}_3\text{K}_9(\text{SO}_4)_6$  ( glaserite)  $\alpha\text{Ca}_3(\text{PO}_4)_2$

Monoclinic cell)	pseudo- orthorhombic cell)	$\beta\text{Ca}_3(\text{PO}_4)_2$	$\text{Na}_3\text{K}_9(\text{SO}_4)_6$	$\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$
<u>a</u> 12.86 Å	20.71*	10.32 Å	9.80 Å	22.84 Å
<u>b</u> 27.33	9.109	10.32	9.80	9.994
<u>c</u> 15.23	15.22	37.0	7.33	17.09
$\beta$ 125°20'		$\gamma:120^\circ$	$\gamma:120^\circ$	$\beta:99.96^\circ$
space group $\text{P}2_1/\text{a}$		$\text{R}3\text{c}$ or $\text{R}\bar{3}\text{c}$	$\text{P}\bar{3}\text{m}1$	$\text{C}2/\text{c}$
Vol. 4367 Å <sup>3</sup>		3412 Å <sup>3</sup>	610 Å <sup>3</sup>	3841
density 2.81 g/ml		3.12 g/ml		3.13 g/ml
Fwt/cell 24		21	1	8
Vol. $\text{M}_3(\text{XO}_4)_2$ 182.0 Å <sup>3</sup>		162.5 Å <sup>3</sup>	203 Å <sup>3</sup>	160 Å <sup>3</sup>

$$* 2 \times 12.86 \cos (125^\circ 20') = 20.98 \text{ Å}$$

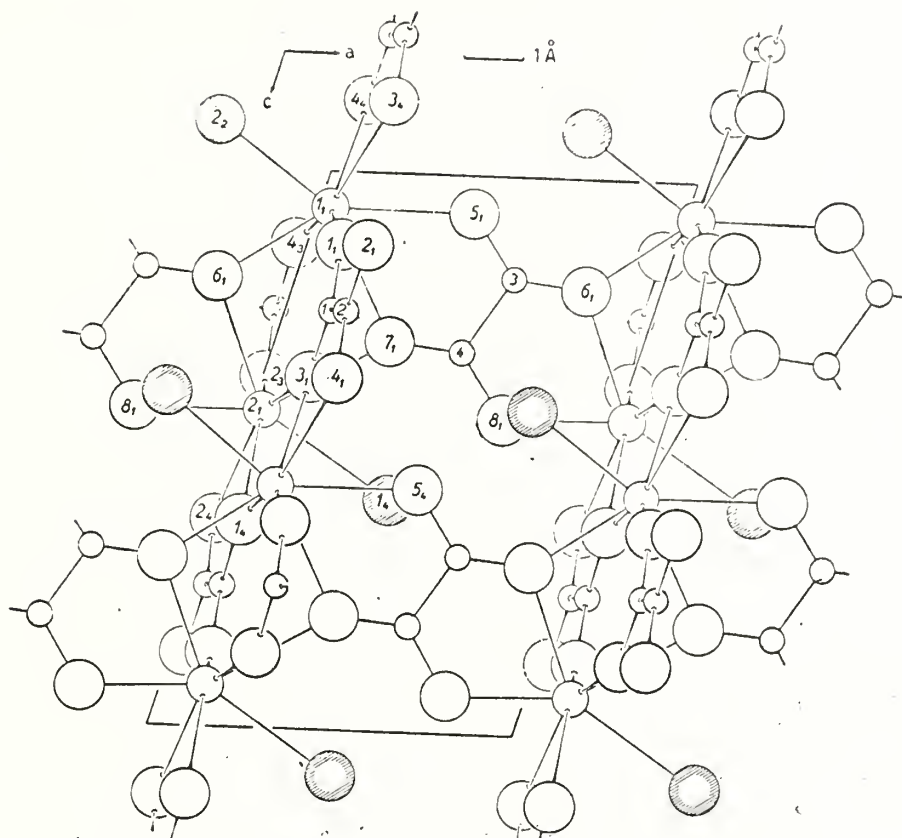


Figure 22. Projection of half of the structure of whewellite on a plane roughly normal to  $[010]$ .

Weddellite is tetragonal with  $\underline{a} = 12.30 \pm .02$ ,  $\underline{c} = 7.34 \pm .02$  and space group I 4/m. Its structure (Sterling, 1965) is shown in Figure 23. For this structure,  $R = 0.13$ . The Ca... oxalate coordination is similar to that in whewellite. An unusual feature in the structure is the O(7) water, which is not in a position to form well defined hydrogen bonds and which is held in a zeolitic manner to a variable extent. The refinement suggests (Sterling, 1965) 0.4 of a water in this position, which in turn suggests the formula  $\text{Ca}(\text{COO})_2 \cdot 2.2\text{H}_2\text{O}$ , close to the measured value of  $2.17\text{H}_2\text{O}$ . Crystallographically, the maximum amount of water the structure can hold is  $2.5\text{H}_2\text{O}$ , which agrees with the suggestion of Philipsborn (1952). The hydrogen positions were not determined but possible hydrogen bonds have been suggested from inter-oxygen distances and angles.

(i) Newberyite  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$

Newberyite is often found with struvite, of which it may be a decomposition product. It is found in various types of guano and in urinary calculi. The structure has been determined (Sutor, 1967) ( $R = 0.044$ ) and is shown in Figure 24. The acid hydrogen has been assigned on the basis of the P-O bond lengths and the O...O distances; the remaining hydrogens have not been assigned unequivocally.

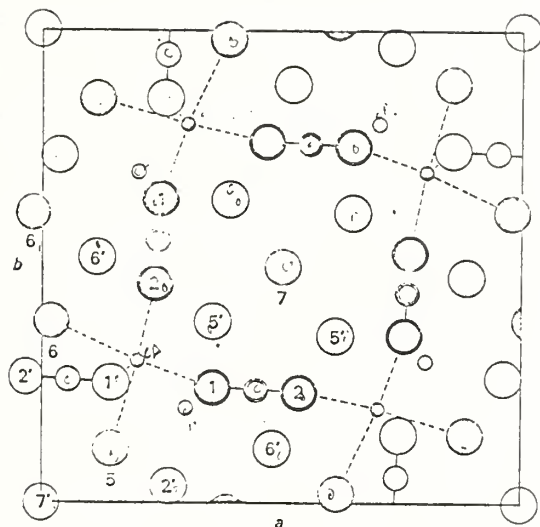


Figure 23. Cell of weddellite. Atoms of primitive cell have bolder outlines or are solid. Smallest atoms are calcium, next larger ones are carbon, and largest are oxygen. Atoms of oxalate groups are connected with solid lines. Broken lines connect calcium ions in primitive cell with the oxygen atoms which they are coordinated. Solid oxygen atoms represent water molecules, 5 and 6 lying in the mirror plane (001). The solid calcium atoms also lie in (001).

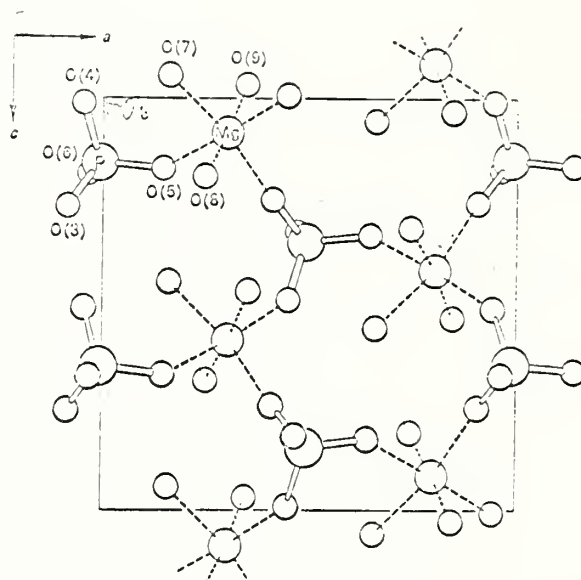


Figure 24. Bounded projection of the structure of  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  from  $y = 0 \rightarrow 0.5$  on (010), showing the magnesium coordination. The magnesium atoms which are approximately coplanar are sandwiched by two planes of phosphorus atoms. In the bounded projection from  $y = 0.5 \rightarrow 1.0$  which completes the structure, the atoms are related to these by  $1/2 - x$ ,  $1/2 + y$ ,  $z$ .

(j) Struvite  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

Struvite is apparently almost ubiquitous, having been found in canned crabmeat, shrimp, lobster, in peat bogs, in a mammoth's tooth and in bat guano. Its structure has been determined (Whitaker, 1965). The magnesium ion is coordinated by water molecules only, as one would expect from the similar situation in  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Baur, 1964). Struvite may be produced in vivo by bacterial action (Palache, 1923; Ayres, 1942). It seems probable that most or all of the newberyite found in calculi results from the decomposition of struvite (Lonsdale and Sutor, 1966).

(k) Calcium Arsenates

We have seen earlier that hydrated salts may be important in general as precursors in precipitation from aqueous solution. In the case of calcium phosphate hydrates, the calcium arsenates are a rich source of structural information by analogy.

Various hydrated calcium arsenates are thought to (See for example, Pierrot (1964) and references therein.) exist./ While several are related to known hydrated calcium phosphates, other have no analogy among the stable calcium phosphates. The structures of these arsenates may shed light on the possible composition of the highly hydrated amorphous phase (or on other possible precursors in the calcium/phosphate/water system.

Table 19

Hydrated Calcium Arsenates

$\text{Ca}(\text{H}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$	$n = 0, 1, 2, 3$
$\text{CaHAsO}_4 \cdot n\text{H}_2\text{O}$	$n = 0, 1, 2, 3$
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot n\text{H}_2\text{O}$	$n = 4, 5, 9$
$\text{Ca}_3(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$	$n = 0, 2, 4, 8, 10$
$\text{Ca}_{10}(\text{OH})_2(\text{AsO}_4)_6$	
$\text{Ca}_2(\text{OH})\text{AsO}_4 \cdot 2\text{H}_2\text{O}$	



Table 20

## Unit Cell Data on Some Hydrated Calcium Arsenates

Formula	Mineral Name	Crystal System	Cell Parameters	Space Group
$\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}^{\text{a}}$	Pharmacolite	m	6.001, 15.58, 114°43'	Ia
$\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$	Haidingerite	o	6.946, 16.14, 7.930	Pcnc
$\text{CaHAsO}_4^{\text{b}}$	Weilite	a	7.11, 6.94, 7.15, 94°19', 101°35', 87°22'	
$\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$		m	22.75, 10.19, 4.81, 97°19'	
$\text{Ca}_3\text{AsO}_4 \cdot 10\text{H}_2\text{O}$	Rouenthalite	t		
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$	Sainfeldite	m	18.64, 9.81, 10.12, 97°	C2/c
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$	Vladimirite	m	5.81, 10.19, 22.7, 82°41'	P2 <sub>1</sub> /c
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$	Guerinite	m		
$(\text{CaMg})_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$	Picropharmacolite	m	13.7, 13.5, 6.75, 100°5'	
$\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	Belovite Talmessite	a	5.89, 7.69, 5.56, 112°38', 70°49', 119°25'	
$(\text{Ca, Co})_2(\text{Co, Mg})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	Roselite	m	5.60, 12.80, 5.60, 100°45'	P2 <sub>1</sub> /c

<sup>a</sup> cf  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (brushite) Structure: Binas, 1966; Cassien, Herpin and Permingeat, 1966.

<sup>b</sup> cf  $\text{CaHPO}_4$  (monetite)

Acknowledgments

Use of the following figures is acknowledged: Figure 4 from Brown (1962); Figures 5 and 6 from Bragg (1924); Figure 7 from Hiriagi, Kachi, Takeda and Nakanishi (1966); Figure 8 from Kahmi (1963); Figure 9 from Bradley, Graf and Roth (1966); Figure 16 from Beevers (1958); Figures 18 and 20 from Jones and Cruickshank (1961); Figure 19 from MacLennan and Beevers (1956); Figure 21 from Greenblatt, Banks and Post (1967); Figure 22 from Cocco and Carobbi (1961); Figure 23 from Sterling (1965); and Figure 24 from Sutor (1967). W. E. Brown is thanked for helpful discussions.

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